

ORGANIC CHEMISTRY OF BIVALENT SULFUR

VOLUME IV

by

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CHAPTER 1.

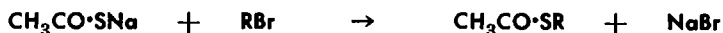
Thioacids

Introduction

A thioacid has an oxygen of its carboxyl group replaced by a sulfur atom, while in a mercapto-acid the -SH group has been substituted for a hydrogen atom. The reactions of thioacids have been reviewed by Tarbell and Harnish.⁶⁷⁹

As one of the oxygen atoms in an acid, such as acetic, is a carbonyl oxygen and the other a hydroxyl oxygen, there should be two different thioacetic acids, which may be called thion-acetic, $\text{CH}_3\text{CS}\cdot\text{OH}$, and thiolacetic, $\text{CH}_3\text{CO}\cdot\text{SH}$.^{523, 549} However, only one acid having the composition, $\text{C}_2\text{H}_4\text{OS}$, is known. Its formula is written $\text{CH}_3\text{CO}\cdot\text{SH}$ and it is commonly called thio-acetic acid. Two arguments have been advanced for this structure: ^{64b}

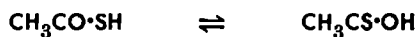
(1) A thiol ester is formed by the action of an alkyl halide on its sodium salt:



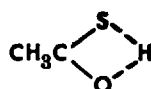
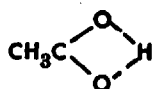
(2) It is readily oxidised to the disulfide by iodine:



These arguments are not conclusive, since the same results would be obtained with an equilibrium mixture of the two tautomeric forms:



An alkyl halide reacts so much faster with a salt in which the metal is joined to a sulfur ⁵⁵⁹ atom than with the corresponding oxygen compound that only the thiol ester would be obtained. The thiol form is the only one that can be oxidised to the disulfide. Acetic acid and thioacetic have been written so that the hydrogen is joined to both oxygen atoms in the one case and to the oxygen and sulfur in the other.^{64a}



Radioactive sulfur has been observed to exchange with the sulfur of thiolacetic acid. The exchange is believed to proceed through the addition of sulfur across the thiocarbonyl linkage.²²⁴

Thionacetic and thionbenzoic acids are supposed to have been isolated,^{478, 612a} but this is not generally accepted. As will be seen below, the isomeric thiol and thion esters are distinct compounds. These and the thioamides are considered here as derivatives of thioacids, though they are seldom prepared from them.

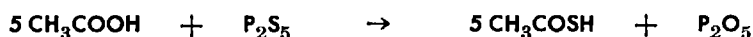
One thioacid, dimethylhydroxythiolerucic, has been isolated from pure cultures of staphylococci.¹⁰⁷

Thioacids

THIOACETIC ACID

Preparation

The first preparation of thioacetic acid was by Kekulé in 1854.^{365a, 366} In his efforts to show the analogies between sulfur and oxygen he heated acetic acid with phosphorus pentasulfide and got thioacetic acid, though in far less amount than is called for by the equation which he so confidently wrote:



With acetanhydride instead of the acetic acid the yield was about 20%.⁶⁹⁷ Schiff added broken glass to control the reaction.⁶²⁰ A mixture of 300 g. phosphorus pentasulfide, 300 g. of acetic acid, and 150 g. broken glass in a 2-liter flask is heated cautiously with a luminous flame. The distillate is collected

until the vapor temperature reaches 103°. The product is redistilled and the cut 92–97° taken. This should be 97–100 g. This method is the one that has been commonly used since that time.^{8, 388, 681a} Recently more convenient methods have been devised.

Thioacetic acid has been obtained from lead acetate and anhydrous sodium thiosulfate.²³⁹ A phenyl ester reacts with sodium hydrosulfide: ^{19, 365b, 641, 719}



Acetyl chloride, saturated with hydrogen sulfide at –15°, gives a 40% yield. Aluminum chloride promotes this reaction.¹³ When an acid chloride is added to pyridine, which has been saturated with hydrogen sulfide, a thioacid is formed. This method has been used for making aliphatic thioacids from thioacetic to thio-caprylic and for thioadipic and thiobenzoic. ^{231, 500, 550} Other acid binding agents may be employed.⁶⁷⁶

Thioacetic acid was obtained conveniently on a fairly large laboratory scale from hydrogen sulfide and acetanhydride containing 20% of acetyl chloride or bromide.¹³⁸ For some unknown reason this method has failed to give reproducible results.^{575c} A semi-works plant was put up to carry out this process, both batchwise and continuously.²⁸⁰ A recent study has shown that the reaction goes best in the presence of an alkaline catalyst. Acetanhydride, containing 2% of sodium sulfide, is shaken with hydrogen sulfide under pressure at 50–60°. The yield is 60–88%. At higher pressures of hydrogen sulfide, acetic acid can be substituted for the anhydride.^{195, 196a} It has been proposed to add acetanhydride dropwise to a cold, stirred solution of sodium hydrosulfide and to set free the acid by dilute sulfuric acid.⁴⁶² In another method, acetanhydride and hydrogen sulfide are passed over activated carbon at 120–60°. ⁴⁶ Acetanhydride and triethylamine may be brought into countercurrent contact with hydrogen sulfide.⁴⁷ Hydrogen sulfide and ketene may be made to unite.^{157,}

316

From a study of all of the proposed methods, the following, which is essentially that of Sjöberg,⁶⁵¹ appears to be the best. Acetanhydride, containing 1% of pyridine, is saturated with hydrogen sulfide. The temperature should be below 20°, preferably around 0°, and the contact should be efficient. The introduction of the gas should be continued until a full equivalent

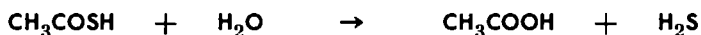
has been absorbed. This can be judged by the gain in weight, or by the increase in volume or in density of the liquid. It should be remembered that the reaction is reversible:



Heating speeds the decomposition and shifts the equilibrium by driving off the hydrogen sulfide. The product should be fractionated through a short column at reduced pressure so that the thioacetic acid comes over below 50°. A second fractionation can be made through a better column. The yield should be above 80%.

Reactions

Thioacetic acid is only moderately stable. Decomposition may begin at 120°. One of the products is carbon oxysulfide.⁴²⁴ Thioacetic acid is hydrolyzed by heating with water:³⁴



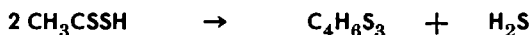
The mechanism of its photolysis has been studied.⁵²

Hydrogen sulfide is given off from a solution of thioacetic acid in liquid hydrogen fluoride. The other product may be acetyl fluoride, but no fluorine compound has been isolated.³⁹³

Heated with zinc chloride, disproportionation seems to take place:

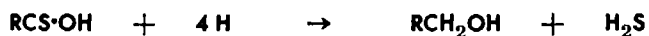


Then hydrogen sulfide is eliminated and a crystalline compound melting at 225° is formed:^{76b}



The molecular formula appears to be $\text{C}_8\text{H}_{12}\text{S}_6$.²⁴² A structural formula analogous to that of hexamethylene tetramine has been proposed.²³⁰ The same product is obtained under the influence of hydrogen bromide¹¹⁶ and when liquid hydrogen sulfide and acetyl chloride are heated in a sealed tube.⁷⁸ Its crystal form is orthorhombic.¹⁸⁰ As a cyclic sulfide it was mentioned previously in Volume III.

The sulfur of thioacetic acid is removed quantitatively by hydrogen peroxide.³⁸⁹ Raney nickel converts a thioacid to the primary alcohol.⁶⁰⁷ This may be regarded as a reaction of the tautomeric thionacetic acid:



The sulfur may be abstracted leaving acetaldehyde.⁸⁴ Hippuraldehyde has been obtained in this way from thiohippuric acid.¹⁵⁴

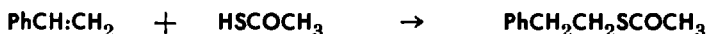
Bromine added to an ether solution of thioacetic acid gives the unstable compound $\text{C}_6\text{H}_{10}\text{Br}_2\text{SO}_2$.¹¹⁶

The addition of thioacetic acid or of its ammonium salt to solutions containing heavy metal ions causes the precipitation of the corresponding thioacetates. A number of these salts have been described.^{681b, 697} Cobalt and ferric thioacetates can be extracted from aqueous solution by an organic solvent such as amyl alcohol. These extracts have characteristic colors, blue for cobalt and red for ferric iron.¹⁶⁵ The heavy metal thioacetates are unstable⁶³⁴ and are hydrolyzed readily into acetic acid and the sulfides of the metals. Or, what amounts to the same thing, the hydrogen sulfide from the decomposition of the thioacetic acid precipitates the metals as sulfides.⁶⁸³ This is the basis of its use in qualitative and quantitative analysis in place of hydrogen sulfide. This has been strongly recommended.^{621, 683} It is far more convenient to add a few drops of a liquid to a solution than to bubble gas through it. This is particularly advantageous in dealing with small quantities of metals.¹³⁷ It has been used for the quantitative precipitation of arsenic sulfide.^{392b, 620, 681a} Thioacetic acid may be determined volumetrically by titrating the zinc sulfide formed from it with permanganate.⁶⁸⁴

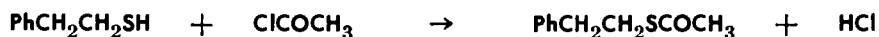
Mixed salts have been prepared, such as MeCOSBiSO_4 , $(\text{MeCOS})_2\text{BiI}$, and MeCOSBiI_2 . Bismuth thioacetate, $(\text{MeCOS})_3\text{Bi}$, m. 85° , boiled with water, gives MeCOSBiS . Various arsenic complexes have been described.^{681c} Mercuric thioacetate-chloride, MeCOSHgCl , is decomposed by water with the formation of aldehyde and acetic acid.⁵⁷² In addition complexes of nickel and zinc salts of thioacids with pyridine, the pyridine N is attached to the metal.⁴¹⁷

In dry ether an addition product is formed with potassium hydroxide.¹⁷⁰

The most interesting reaction of thioacetic acid is its ready addition to unsaturates.^{31, 99, 108a, 160, 196b, 303, 335} An example of this is its addition to acrylonitrile.^{158a} In this it exhibits its mercaptan character, but in activity it far surpasses most mercaptans. Usually the addition takes place spontaneously and completely. With styrene the reaction is:³⁵⁷



The product is the β -phenethyl ester of thioacetic acid and is identical with that from phenethyl mercaptan and acetyl chloride: 314c, 360



The addition goes contrary to Markownikow's rule. The addition of hydrogen sulfide, which was mentioned in chapter 1, Volume I, looks much simpler but is far more difficult to effect. As the thioacetic acid addition product is an ester which is easily hydrolyzed to a mercaptan, this is a choice way of preparing a mercaptan. As has been mentioned in chapter 5, Volume I, many mercapto-acids have been made from the addition products of thioacetic acid to unsaturated acids.^{215, 229, 316, 542b, 623}

With butylacetylene, the addition takes place in two stages to form BuCH:CHSAc and $\text{BuCH(SAc)CH}_2\text{SAc}$.³² With phenylacetylene, only one product, PhCH:CHSAc , is formed.^{315d} With butadiene, it goes in two stages.¹⁵⁹

The addition of aliphatic thioacids to Diels-Alder adducts gives bicyclo(2,2,1) heptane derivatives.⁹²

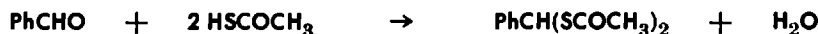
Thioacetic acid, anthracene, and oxygen give the diacetyl derivative of 9,10-dimercapto-9,10-dihydroanthracene. The disulfide, MeCOS:SCOMe adds in the 9 and 10 positions.⁴⁹¹

Thioacetic acid has been added to 2-phenyl-4-benzilidene-5(4H)oxazolone and to its isopropylidene analog.⁴⁵⁷ Thioacetic acid can be added to unvulcanized rubber.^{187a} By adding thioacetic acid to a polymer, such as natural rubber, and hydrolyzing the acetyls, mercapto groups are left on the polymer.³³⁴

Ethylene oxide reacts with thioacetic acid to give the β -hydroxyethyl ester, $\text{CH}_3\text{COSCH}_2\text{CH}_2\text{OH}$. When this is heated with water it isomerizes to the mercaptan, $\text{CH}_3\text{COOCH}_2\text{CH}_2\text{SH}$, which gives a mercury mercaptide, $(\text{CH}_3\text{COOCH}_2\text{CH}_2\text{S})_2\text{Hg}$.⁵²¹ This is a case of alcoholysis in which an alcohol replaces a mercaptan. With epichlorhydrin the product is $\text{CH}_3\text{COSCH}_2\text{CH(OH)CH}_2\text{Cl}$.⁶⁵¹

On mixing thioacetic acid (or other thiol acid) and ethylene imine, the amide, $\text{CH}_3\text{CONHCH}_2\text{CH}_2\text{SH}$, is formed, which can be readily hydrolyzed to the aminomercaptan.^{32.3, 32.4}

The mercaptan nature of thioacetic acid is shown by its reaction with an aldehyde: 46.3, 76a

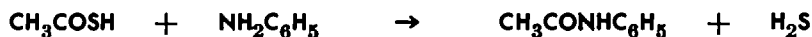


Thioacetic acid distilled at atmospheric pressure with triethyl amine gives $(\text{MeCOS})_2\text{CHMe}$.^{46,3} The formation of thiobenzophenone by the action of thioacetic acid on diphenylmethylen chloride may involve a similar intermediate:⁶³⁰



This has been discussed in volume III under Thioketones and under Mercaptals and Mercaptoles.

Thioacetic acid reacts rapidly with aromatic amines:



It is necessary to boil α -naphthylamine for several days with acetic acid to prepare its acetyl derivative, but with thioacetic acid the reaction is spontaneous and complete.⁵³⁹ As acetylation takes place, even in aqueous solution, it may be regarded as a model of the biological alkylation of coenzyme-A.⁶³⁸ Instead of the free acid its phenyl ester may be used. It acetylates pantotheine³⁸⁶ and glutathione.⁷²⁹

Thioacids, or their phenyl esters, have been employed in building up polypeptides.^{154, 645, 733} Thus two molecules of phenyl thio-glycine condense:



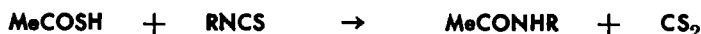
This used with valine gives diglycylvaline.⁷³² Ethyl trifluorothioloacetate has been used to introduce the trifluoroacetyl group into amino acids and peptides.⁶¹⁶

Thioacetic acid reacts with cyanoguanidine to give a high yield of methyliminothiotriazine.⁵²⁹ These reactions are related to those discussed in a later section on the biological importance of thiol esters.

Thioacetic acid combines with a thiocyanate to give a dithio-urethane which loses thiocyanic acid, leaving a thiol ester;



With an isothiocyanate a substituted amide is formed:



This is a general reaction for aromatic as well as aliphatic thioacids.^{351, 723c, 725, 726}

Thioacetic acid gives an abnormally small molecular lowering in freezing acetic acid.^{26, 103} Substitution of the -SH group for the -OH of an acid increases the dissociating power and about doubles the dielectric constant, which for thioacetic acid is 12.8°. ^{704a} A later value is 17.3° at 21°. ¹⁹⁴ The mobility of the thioacetic anion has been measured. ⁴⁵⁰ The specific conductivity of this acid in liquid hydrogen sulfide is 2.96×10^7 . ⁵⁵⁸ The conductivity of tetraethyl ammonium iodide in thioacetic acid has been measured. ^{256, 704b} The infrared ^{156, 264} and Raman ⁶⁸⁶ spectra have been studied. The magnetic susceptibility is 418×10^{-7} and the diamagnetic susceptibility, -38.40×10^{-6} . ⁵³⁶ The latter indicates the thiol structure, $\text{CH}_3\text{CO}\cdot\text{SH}$, for the acid without any resonance in the carbonyl group. ^{142b} The absorption curves agree with this structure for the acid but point to a mixture of thiol and thion forms for the potassium salt. ²⁸⁹ The ultraviolet absorptions of CH_3COSH , ClCH_2COSH , Cl_2CHCOSH , and Cl_3CCOSH have been compared. ^{64b, 400} The distribution of thioacetic acid between ether and water at 25° is 1 : 0.84. ⁶⁵⁴

Thiobetaine has an amphoteric polar structure. ¹⁸¹

Thioacetic acid increases the liberation of iron from the hemoglobin of the blood. ⁶⁴⁸ Its magnesium salt has been suggested as an antidote in mercury poisoning. ¹⁷⁶ The strontium salt has been recommended for chronic lead and mercury poisoning. ⁴⁵⁵ Thioacetic acid lowers the blood sugar in rabbits. ⁶⁰⁵ The lethal dose for mice is 0.125 mg. per gram of body weight. ⁶¹

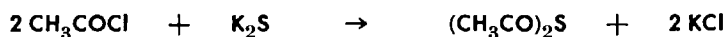
Thioacetic acid has been claimed as a promoter of separation in flotation ⁵⁰² and as a fumigant against the rice weevil. ⁵⁹⁵

Acetyl Sulfide

By heating acetanhydride with phosphorus pentasulfide, Kekulé got acetyl sulfide, $(\text{CH}_3\text{CO})_2\text{S}$. ^{45, 365a} It was later made by heating lead thioacetate to 150°: ³⁶⁶



Acetyl chloride reacts with potassium sulfide: ³⁴³



It was obtained also from bismuth and arsenic salts. ^{681c} All of these preparations boiled at 120–1° and were not pure. The pure compound has been made from lead thioacetate and acetyl chlo-

ride.¹⁶⁶ It is formed in 90% yield when thioacetic acid and acetyl chloride are refluxed together.⁷⁷ Similarly, chlorothioacetic acid and chloroacetyl chloride give the sulfide, $(\text{ClCH}_2\text{CO})_2\text{S}$.¹³ Acetyl sulfide is formed by the action of liquid ketene on liquid hydrogen sulfide,^{130, 169} or when they are passed over an alumina catalyst in gaseous form.¹⁵⁷ Bubbling ketene through thioacetic acid at 60° gives the anhydride.^{158b} Only symmetrical compounds of this type are stable.^{91b} The possibility of an acetyl sulfide was considered by Berzelius.⁵⁸

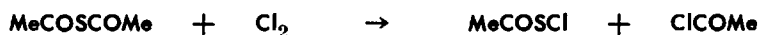
Acetyl sulfide is insoluble in water and not affected by cold water, but in hot water, it is hydrolyzed to acetic and thioacetic acids.¹⁶⁶ It is oxidised by nitric acid to acetic and sulfuric acids.⁶¹⁴ Raney nickel reduces it to acetaldehyde.⁷⁷

Acetyl disulfide, $(\text{MeCO}_2)_2\text{S}_2$, is obtained by treating thioacetic acid with iodine³⁶⁶ and also by electrolysis.¹⁰⁵ It is reduced to the acid by sodium arsenite. It gives up sulfur to potassium cyanide.²⁷⁷

Acetyl trisulfide, $(\text{MeCO}_2)_2\text{S}_3$, has been made from acetyl chloride and hydrogen trisulfide with zinc chloride. It is unstable, and is decomposed by water into acetic and thioacetic acids and hydrogen sulfide.⁶⁵

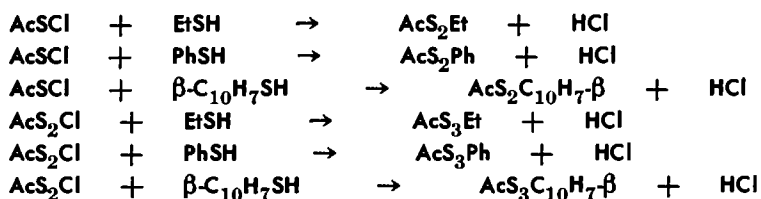
Silver acetate and sulfur dichloride give the disulfide, $(\text{CH}_3\text{COOS})_2$ which, on standing, decomposes into acetanhydride and sulfur dioxide.¹⁷⁵

Acetyl sulfide has been chlorinated in carbon tetrachloride at -15° . The primary reaction seems to be:



Higher sulfur compounds, MeCOS_xCl , are also formed. Benzoyl tetrasulfide gives PhCOS_2Cl and PhCOS_4Cl .⁷¹ Chlorination of acetyl disulfide, under similar conditions, gives the disulfide chloride, AcS_2Cl . This adds to ethylene to form $\text{AcS}_2\text{CH}_2\text{CH}_2\text{Cl}$, b_{10} $118-20^\circ$.⁷²

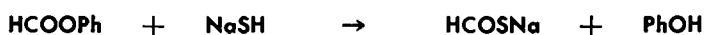
These acyl sulfur chlorides react with mercaptans: ^{72, 74.5}



Analogous benzoyl derivatives are obtained similarly. These go up to BzS_4Cl and BzS_5R .⁷²

THIOFORMIC ACID

Thioformic acid has not been isolated. The action of sodium trithiometaphosphate, NaPS_3 , on formic acid gives a product which seems to contain a thioacid. From phenyl formate the sodium salt is obtained: ^{18b}



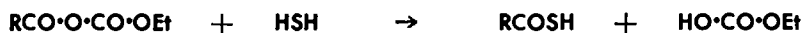
Its hydroxylamine derivative, $\text{HC}(:\text{NOH})\text{SH}$, is formed by the action of hydrogen sulfide on mercury fulminate,^{114b, 512} and from chloroform with sodium sulfide and hydroxylamine.^{114b} It decomposes in two ways:



OTHER THIOACIDS

Thiopropionic acid has been made by the phosphorus pentasulfide method.³⁸⁸ So have thio-*i*-butyric, and thio-*i*-valeric.⁶⁹⁷ Thiopropionic acid has been prepared by the Grignard reaction using carbon oxysulfide.⁷¹⁴ Thiomyristic and thiopalmitic acids have been prepared from the phenyl esters.¹⁹ Chlorothioacetic acid has been made from the acid chloride and hydrogen sulfide in the presence of aluminum chloride.¹³ 1-Phenylcyclopentanethiocarboxylic acid is obtained from the reaction of the acid chloride with potassium hydrosulfide. With potassium sulfide, the product is the thioanhydride. The acid is oxidised to the disulfide by ferric chloride.⁴⁴¹ Thiocamphoric acid has been prepared from the anhydride and sodium trisulfide.⁵⁸⁹ An optically active thioacid, *D*-MePrCHCOSH, has been studied along with the *L*-acid.⁴³⁶

An efficient general method of preparing thioacids is the reaction of hydrogen sulfide on the mixed anhydride, $\text{RCO}\cdot\text{O}\cdot\text{CO}\cdot\text{OEt}$, in the presence of a tertiary amine: ^{154, 645, 732, 733}



The unstable monoethyl carbonate does not interfere.

A highly branched thioacid can be obtained by the alkaline hydrolysis of the trithione from diisobutylene.⁶⁶²

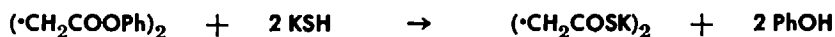
Several thio amino acids, such as thio- β -alanine, thioglycine,

thioalanine, thiovaline, thioisoleucine, and thiomethionine, have been prepared by the reaction of the thiophenol ester with hydrogen sulfide.^{731, 735}

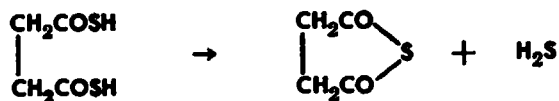
DIBASIC *bis*-THIOACIDS

bis-Thio-oxalic acid, $(\text{COSH})_2$, has received attention on account of its ability to form highly colored double salts such as: ^{356, 597} $\text{K}_2\text{Ni}(\text{COS})_4$, $\text{BaNi}(\text{COS})_4 \cdot \text{H}_2\text{O}$, $\text{PbNi}(\text{COS})_4 \cdot 2 \text{H}_2\text{O}$, $(\text{NH}_4)_2\text{Ni}(\text{COS})_4 \cdot 4 \text{H}_2\text{O}$, $\text{Na}_2\text{Ni}(\text{COS})_4 \cdot 2.5 \text{H}_2\text{O}$, $(\text{PhNH}_3)_2\text{Ni}(\text{COS})_4$, $\text{K}_2\text{Pd}(\text{COS})_4$, $\text{BaPd}(\text{COS})_4 \cdot 3 \text{H}_2\text{O}$, $(\text{PhNH}_3)_2\text{Pd}(\text{COS})_4$, $(\text{PhNH}_3)_2\text{Fe}(\text{COS})_4 \cdot \text{H}_2\text{O}$, $\text{BaKCo}(\text{COS})_6 \cdot 4 \text{H}_2\text{O}$, $\text{K}_3\text{Co}(\text{COS})_6 \cdot 2 \text{H}_2\text{O}$, $(\text{PhNH}_3)_3\text{Co}(\text{COS})_6 \cdot 2 \text{H}_2\text{O}$. From the barium salt, the complex acid, $\text{H}_2\text{Ni}(\text{COS})_4 \cdot 4 \text{H}_2\text{O}$, can be prepared. Its solution has a higher conductivity than one of sulfuric acid of the same normality. The palladium complex acid, $\text{H}_2\text{Pd}(\text{COS})_4 \cdot 3 \text{H}_2\text{O}$, is similar.^{355a} The nickel-potassium salt is isomorphous with the corresponding platinum and palladium complexes. They all appear to have planar configurations.^{150a} This nickel salt has a magenta color and can be used for the colorimetric detection and determination of nickel.^{213, 265, 510} The best results are with a 0.05% solution of the potassium salt, $\text{K}_2\text{C}_2\text{O}_2\text{S}_2$, and a nickel concentration of 10 mg. per liter.⁷⁶² The potassium nickel dithiomalonate is also colored and can be detected in 4,000,000 parts of water, which is to be compared with 40,000,000 for the corresponding dithio-oxalate.^{355b}

Phenyl succinate reacts with potassium hydrosulfide: ⁷¹⁹

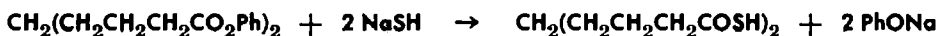


The free acid loses hydrogen sulfide:



This is soluble in water and alcohol. From succinyl chloride and sodium sulfide, the same compound has been obtained.^{18a, 719} This is identical with the product from succinic acid and phosphorus pentasulfide.^{18a} It gives a diphenylhydrazide with phenylhydrazine.⁷⁶⁸

Diphenyl azelate reacts similarly:



The disulfide, which is an oil, is obtained from the sodium salt and iodine.⁸²

Dithioacids from dithiomalonic to dithiosebacic,^{41.5, 356, 675, 676} and many others,⁴¹⁴ have been prepared from the acid chlorides and hydrogen sulfide in pyridine. These acids, like their monobasic analogs, combine with unsaturates to give the abnormal addition products. With simple olefins, the addition is catalyzed by peroxides, while with conjugated systems it is base-catalyzed.^{41.5}

A monothio dibasic acid is formed when sodium hydrosulfide reacts with the anhydride of succinic, or glutaric, acid.⁴¹⁴

AROMATIC THIOACIDS

The best known aromatic thioacid is thiobenzoic, which has been made from benzoyl chloride and potassium hydrosulfide.^{141, 227, 243, 299, 421, 575a, 646}

Its preparation has been described recently.^{518b} The *p*-fluoro-²²⁶ and *p*-nitro-^{286, 371, 421} acids have been made similarly. Magnesium hydrosulfide, from ethyl magnesium bromide, has been substituted for the potassium hydrosulfide.⁴⁹⁴ Thiobenzoic acid also has been prepared by the Grignard reaction, using carbon oxysulfide.^{64a}

Thiofuroic⁵³⁸ and thionicotinic^{70, 269} acids have been made from the chlorides and sodium hydrosulfide. This is a general method.^{441, 645, 685} Treating a mixed aromatic-aliphatic anhydride with hydrogen sulfide gives the aromatic thioacid.¹⁵⁴

Thiobenzoic^{575c} and thiofuroic⁵³⁸ acids go to the disulfides, (ArCOS)₂, on exposure to air. Thiobenzoic acid has been oxidised to the disulfide by iodine,^{64a, 227, 498} by hydrogen peroxide,^{498, 646} by ferric chloride,⁴²¹ by sulfur monochloride,^{125a} by ferricyanide,²⁴³ by triethyl amine,^{46.3} and by electrolysis.¹⁰⁵ Thionicotinic acid gives the disulfide with iodine.⁷⁰ The acid disulfides can be obtained directly from the acid chlorides and sodium disulfide^{36, 87, 245} or hydrogen disulfide.⁶⁵ *p*-nitrothiobenzoic acid can be oxidised to the disulfide by ferric chloride.³⁷¹ From *bis*-thioterephthalic acid, the polymeric disulfide has been obtained by oxidation with iodine.⁴¹⁴

On heating, benzoyl disulfide decomposes. Some of the products are benzoic acid, sulfur, hydrogen sulfide, and probably

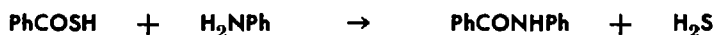
tetraphenylthiophene.²⁴³ With potassium hydroxide, it gives potassium benzoate, thiobenzoate, and sulfur,²⁴⁰ while with ammonia the products are benzamide, ammonium thiobenzoate, and sulfur.^{111, 240}

Benzoyl chloride and sodium sulfide give the monosulfide, or thioanhydride, $(\text{PhCO})_2\text{S}$.^{53, 62, 243} An important by-product is $\text{PhCH}(\text{SCOPh})_2$, which can be made also from the acid and benzaldehyde.⁵³ From benzoyl chloride and hydrogen sulfide in pyridine, one author reports the thiobenzoic acid, PhCOSH ,⁶⁷⁶ and another the dithioanhydride, $(\text{PhCS})_2\text{O}$.⁴⁴³ Phthalic anhydride and sodium sulfide give the thioanhydride, $\text{C}_6\text{H}_4(\text{CO})_2\text{S}$.⁵⁷⁸ Phthaloyl chloride gives a mixture of products,^{125b, 245} one of which is supposed to be the disulfide.^{125b} From pyromellitic acid and sodium sulfide, the dithioanhydride, $\text{S}(\text{CO})_2\text{C}_6\text{H}_2(\text{CO})_2\text{S}$, is obtained.⁵³¹ The polymeric thioanhydride from *bis*-thioterephthalic acid has been made from the acid chloride.⁴¹⁴ From acetyl chloride and thiobenzoic acid, a mixed thioanhydride, $\text{PhCO}\cdot\text{S}\cdot\text{COMe}$, is obtained.⁴⁹⁴

Benzoyl chloride and hydrogen trisulfide give the disulfide instead of the trisulfide, but the trisulfide may be gotten from potassium thiobenzoate and sulfur dichloride. Phenylacetyl trisulfide is obtained from the chloride and hydrogen trisulfide. It loses a third of its sulfur readily.⁶⁵

Phthalide and sodium hydrosulfide give either the thiophthalide or *o*-carboxybenzyl disulfide.²⁰

Thiobenzoic acid, like thioacetic, reacts with aniline:



This reaction is many times more rapid than the corresponding reaction with benzoic acid.^{518a} A kinetic study has been made of this reaction.²⁹⁹

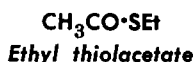
Thiophenylacetic acid, PhCH_2COSH , can be made in the same ways as thiobenzoic. The free acid is oxidised by air to the disulfide, which can also be made from the sodium salt and iodine.³⁵¹

Nickel carbonyl is formed by the action of carbon monoxide on nickel thiobenzoate.³⁰⁴

Addition of a small proportion of a monothiol acid to natural rubber decreases the tendency to crystallize at low temperatures.^{590.5}

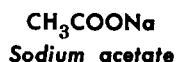
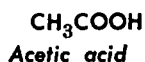
Esters of Thioacids

As was mentioned in the introduction, there are two isomeric esters of a thioacid, though the acid is known in only one form.



Neither of these is regularly made by the direct esterification of thioacetic acid and neither gives the thioacid on saponification, yet they are considered in this chapter on account of formal relationships.

Traditionally esters are named as derivatives of the acids along with their salts. In the early days of structural chemistry, ethyl acetate was regarded as acetic acid in which the hydroxyl hydrogen had been replaced by the ethyl radical. This made it look like sodium acetate.



In the chemical literature of the last century esters were frequently called "ethereal salts." In French "ether-sels" has lingered. In his lectures Remsen habitually used that term.

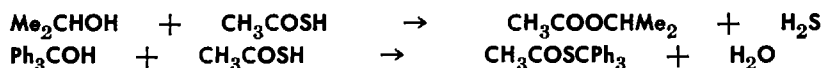
It is now recognized that ethyl acetate is ethanol in which the hydroxyl hydrogen has been replaced by the acetyl group and should be called acetylethanol. The study of the esterification of mercaptans was an important factor in establishing this view.^{575a} Ethyl thioacetate is the acetyl derivative of mercaptan.

Both thiol and thion esters of organic acids will be considered in this chapter, while esters of inorganic acids have been taken up in chapter 3, volume I.

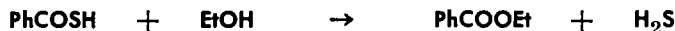
THIOLESTERS, RCOSR'

Preparation

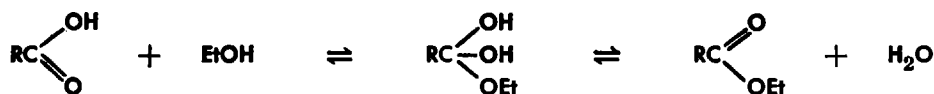
Whether hydrogen sulfide or water is eliminated in the esterification of an alcohol by thioacetic acid depends on the nature of the alcohol. Normally hydrogen sulfide is given off and the product is exclusively, or predominately, the oxygen ester. When the hydroxyl of the alcohol is labile, as it is in triphenylcarbinol, a thiol ester may be formed:



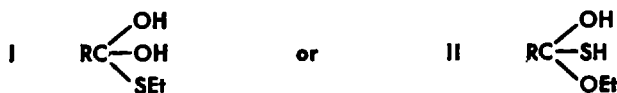
With methanol, or ethanol, 78% of the ester is acetate and 22% thioacetate.⁶⁷³ The *bis*-thioacetate, $\text{OC}(\text{NHCH}_2\text{SCOMe})_2$, is formed from dimethylolurea.^{108b, 187b} It has been known for a long time that the esterification of thiobenzoic acid gives a sulfur-free ester:



According to Henry's hypothesis, the first step in esterification is the addition of the alcohol to the acid to form an intermediate from which water is eliminated:

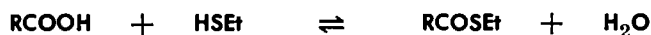


With a mercaptan the intermediate would be either:



Which of these is formed would depend on whether the mercaptan divides into EtS-H or Et-SH in the adding. Intermediate I could lose only water, while II could lose either water or hydrogen sulfide. Experiment showed that ethyl thiolbenzoate is the product from benzoic acid and mercaptan. This was taken as implying that ethanol divides EtO-H and that the oxygen of the alcohol enters the ester.^{575a} Later experiments with an alcohol containing O^{18} confirmed this view.⁵⁹⁶

The esterification of ethyl mercaptan by acetic, propionic, or benzoic acids proved to be reversible:



The esterification limits, for equivalent amounts, were determined for several mercaptans and found to be in the same order but much lower than for the corresponding alcohols. Some of the results are in Table 1.1.

The limit is considerably higher with methyl mercaptan than with ethyl and propyl, which are about equal.^{211, 553} With the three toluic acids and ethyl mercaptan, the velocities are quite different but the limits are nearly the same.⁶¹¹

Similar relationships hold in esterification with alcohols. There are great differences in the esterification velocities, but the limits are practically the same, usually slightly higher for the slow

TABLE 1.1
Esterification Limits

	<i>Benzoic Acid</i> ⁵⁵³		<i>Acetic</i> ²¹¹	<i>Propionic</i> ²¹¹
Temperature	220°	243°	200°	200°
	%	%	%	%
MeSH	18.7	19.6	16.2	15.3
EtSH	14.7	15.4	13.0	11.6
PrSH	14.1	15.1	12.7	11.3
<i>i</i> -BuSH	—	12.7	12.1	10.9

acids. With benzoic acid at 200° the limit, 8.9%, for *s*-butyl mercaptan is much lower than the 14.4% for *n*-butyl and 13.6% for *i*-butyl.³⁷⁵

TABLE 2.1
Percentage Esterification by Ethyl Mercaptan

<i>Acid</i>	<i>1 Day</i> %	<i>2 Days</i> %	<i>16 Days</i> %
<i>o</i> -Toluic	1.94	2.65	14.01
<i>m</i> -Toluic	6.98	8.81	13.33
<i>p</i> -Toluic	3.03	4.27	13.36

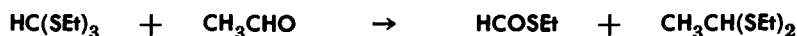
The limits are so low that it is not practicable to esterify the mercaptans without removal of the water. The esterification of a mercaptan by an acid, with sulfuric acid as catalyst and water take off, is claimed.^{5a} Little is known about catalysts for this esterification. Sulfuric acid seems a poor choice since it oxidises mercaptans to disulfides. The esterification of mercaptans of six and of seven carbon atoms by *p*-nitrobenzoic acid is claimed.^{482a}

Various other ways of making thio-esters have been found.⁷³³ An important one is the addition of thioacetic acid to an olefin, mentioned earlier.

Ethyl thiolformate results from the reaction of sodium mercaptide with phenyl formate: ⁶⁴¹



It can be obtained from a trithio-orthoformate and an aldehyde: ^{551a}



An imino ester, from which a thiolformate may be obtained by hydrolysis, is formed from a mercaptan and hydrocyanic acid in the presence of hydrogen chloride: ³²⁴



The hydrolysis is effected by dilute hydrochloric acid: ⁷¹⁰

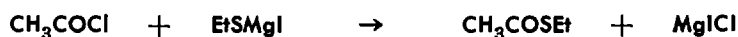


Thiolacetates have received the greatest attention. The first was supposed to have been made by Kekulé ^{365a} by heating ethyl acetate with phosphorus pentasulfide, but his product boiled at 80° instead of 116°. This method has given better results with the chloroacetates. ⁴⁸⁴ A mercaptan reacts readily with an acid chloride: ^{13, 255, 476, 479, 490}

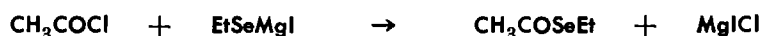


The chlorides of perfluoro ²⁹⁷ and of steroid acids ^{439, 440, 465} react satisfactorily with mercaptans. Unless the mixture is well cooled, a volatile mercaptan may be carried away by the hydrogen chloride that is evolved. The acetyl chloride is added slowly to the strongly cooled mercaptan. The mixture is kept cold for a time and then let stand at room temperature for several days. ^{35, 715} It may be heated eventually. This is a general method for aliphatic and aromatic acid chlorides with mercaptans of both classes. ^{24, 49, 164, 167, 168, 228, 255, 267, 359, 500, 532, 533, 610a, 622} The reactants may be mixed in pyridine. ^{95, 270, 279, 387, 425, 743b} Tributylamine has been mixed with the very volatile methyl mercaptan before adding the acetyl chloride. ⁵⁶⁵ Sodium mercaptide may be substituted for the free mercaptan. ^{456, 614} A mercury mercaptide has been so used. ⁵⁸⁶ Lead mercaptides have been caused to react with acetyl chloride ^{504, 522, 743b} and with benzoyl chloride. ^{201, 522} The lead mercaptide is precipitated from alcohol solution, washed with ether, and dried in a vacuum desiccator. It is

treated with cold acetyl chloride in a flask immersed in an ice-salt mixture.⁵⁸⁷ The mercaptan may be made to react with a Grignard reagent and then with acetyl chloride:^{302, 677}



Selenolesters may be made similarly:⁶⁷⁷

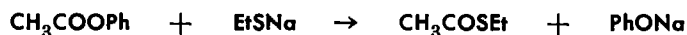


The para-nitro benzothiol ester of vitamin B₁ has been prepared using para-nitro benzoyl chloride and the vitamin.⁴⁷⁹ Chlorides of aminoacids have been used with mercaptans^{327, 732} and amino-mercaptans with acid chlorides.^{191, 329, 406, 729} The mercaptan may be refluxed with acetanhydride containing sodium acetate.^{228, 715} This is suitable for high boiling mercaptans.⁷¹⁵ Zinc chloride is added when the mercaptan is tertiary.³⁰⁶ The mercaptan may be dissolved in 33% sodium hydroxide to which shaved ice and a slight excess of acetanhydride are added. The mixture is stirred vigorously for five minutes and the ester separated. This method is suitable for the lower mercaptans which are readily soluble in aqueous alkali.⁷¹⁵ The bis-thioacetate of trimethylene dimercaptan has been prepared by refluxing it with acetanhydride and a catalytic amount of pyridine.⁵⁷¹ Liquid ketene and mercaptan, kept at -80° for 3 days, give a high yield of the thiol ester:^{32.4, 157, 330}

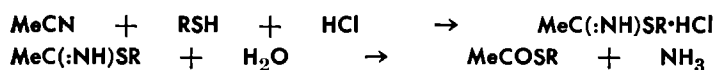


Ketene reacts with the mercaptans in petroleum distillates.¹⁵ It may be used in the presence of an organic acid anhydride and a catalytic amount of sulfuric acid.¹⁸⁶

Phenyl acetate, like phenyl formate, reacts with sodium mercaptide:⁶⁴¹



Thiolacetates are made from tertiary butyl and dodecyl mercaptans and nitriles by forming the iminoesters and hydrolyzing:³⁰⁶



This method has been used for thiolbenzoates.²⁴⁷ From a dinitrile, such as adiponitrile, and a dimercaptan, a linear polymer may be obtained.¹⁴⁴

Acetylation of thiophenol, under Friedel-Crafts conditions, gives the thiolacetate, PhSAc, instead of the acetylthiophenol, AcC₆H₄SH.²⁸

Acetyl chloride and ethylene sulfide give β-chlorethyl thioacetate, MeCOSCH₂CH₂Cl.⁴ A thiolester can be obtained from isobutylene sulfide and acetanhydride and from isobutylene oxide and thioacetic acid, though in the latter case it is not the sole product.¹⁶⁷

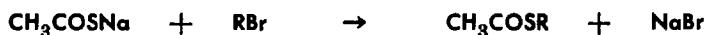
The phenyl ester of chlorothiоlactic acid can be obtained from chloracetyl chloride with thiophenol and cold aqueous alkali.¹⁶⁴ The ester, EtSCH₂COSEt, resulted when both chlorine atoms were caused to react.⁵⁵⁷

The γ-thiolactone of valeric acid has been prepared from the lactone and phosphorus pentasulfide. Some of it went on to the dithiolactone.²³⁸

A thioanilide and an alkyl halide form an iminoester which may be hydrolyzed to a thiolester: ^{705d, 706}

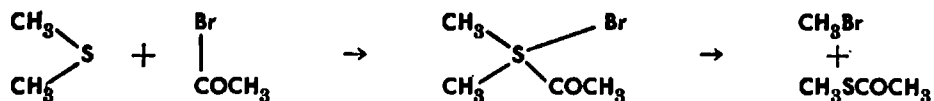


An important method of preparing thiolesters is the reaction of an alkyl halide with the salt of a thioacid: ⁵³⁵



This has been of service in preparing thioacetates of carbohydrates from bromine derivatives.^{617, 618, 637} As the thioacetates are readily hydrolyzed, this is a method of obtaining mercapto-carbohydrates. Other mercaptans have been prepared in this way.^{492, 525, 535} This is a convenient way to make the thiobenzoates.^{22, 226, 243, 269, 285, 286, 375, 553, 575a, 611, 718b, 724} It has been used for making esters of thionicotinic acid.²⁶⁹

An alkyl sulfide heated with acetyl bromide, or iodide, gives a thiolester, probably by way of a sulfonium compound: ^{112b, 276, 522}



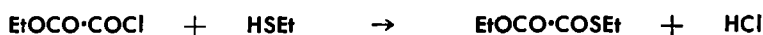
Thioacrylic esters, CH₂:CHCOSR,³⁴⁰ may be prepared from acetylene, carbon monoxide, and a mercaptan.⁵⁸¹ Thioesters of methacrylic acid have been prepared through the acid chloride.⁴¹³

A curious case is the self-esterification of thiosalicylic acid, o-mercaptobenzoic acid. When it is treated with phosphorus

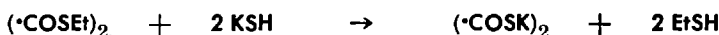
pentoxide cyclic esters are formed from two, three, or four molecules: ³⁷



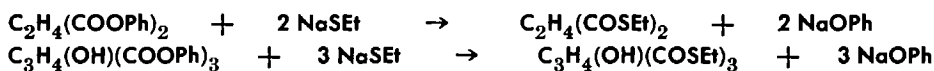
Lauryl monothiosuccinate, $\text{HO}_2\text{CCH}_2\text{CH}_2\text{COSC}_{12}\text{H}_{25}$, can be obtained from succinic anhydride and lauryl mercaptan.²²⁸ 1,6-Hexamethylenedithiol reacts with two molecules of succinic, glutaric, and phthalic anhydrides to give esters of the corresponding monothioacids.⁴¹⁴ A monothio-oxalate ester can be prepared from the ester chloride: ⁴⁹⁹



Oxalyl chloride and mercaptans, or mercaptides, give esters of dithio-oxalic acid.^{433, 667} With alcoholic potassium hydrosulfide these yield potassium dithio-oxalate:



Similarly from malonyl chloride and from succinyl chloride, dithioesters $\text{CH}_2(\text{COSEt})_2$, $\text{CH}_2(\text{COSPh})_2$, $(\cdot\text{CH}_2\text{COSEt})_2$, and $(\cdot\text{CH}_2\text{COSPh})_2$ are obtained. These esters are colored. This may indicate the presence of some of the tautomeric form which contains the strong chromophore :C:S .⁵⁵⁷ The ethyl thiolesters of succinic and citric acids have been made from the phenyl esters and the mercaptide: ⁶⁴¹



By a remarkable reaction diethyl tetrafluoro-*bis*-thiosuccinate is formed from the mercaptan and perfluorobutyrolactone: ²⁹⁶



The addition of bithio dibasic acids to olefins has been reported; *bis*-thioglutaric and *bis*-thiosuberic acids added to cyclohexene to give the dicyclohexyl esters.¹⁶⁰

Polymeric thioesters have been prepared by the addition of dibasic thioacids, such as thioadipic, to diallyl and by the reaction of acid chlorides on dimercaptans with,⁴⁷⁴ or without, pyridine.^{223, 738b} A polymeric trimethylene thiophthalate had been

made much earlier but had not been recognized as such.²² The formation of such polymeric esters by the addition of *bis*-thioadipic and *bis*-thiosuberic acids to biallyl has been examined to find the relations of the properties of the polymers to the conditions in emulsion polymerization.^{414, 475a} With *bis*-thioaromatic acids the slow addition reaction was overshadowed by the rapid oxidation.^{414, 475b}

When phthalic anhydride and thiophenol are heated together and the product treated with phosphoric anhydride, two products are formed which appear to be the symmetrical and unsymmetrical derivatives:¹²⁸



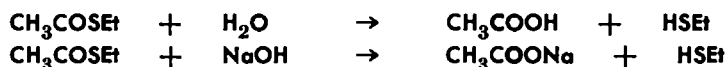
The unsymmetrical one is obtained from phthaloyl chloride with lead phenyl mercaptide⁶⁹⁵ or with phenyl thioacetate and aluminum chloride.³⁹⁷

Phthalic thioanhydride and sodium sulfide unite to form sodium *bis*-thiophthalate, $\text{C}_6\text{H}_4(\text{COSNa})_2$, which can be alkylated to the esters, $\text{C}_6\text{H}_4(\text{COSR})_2$. The thioanhydride, a sodium alkylate, and an alkyl halide give the unsymmetrical ester:⁵⁷⁸



Reactions

A thiol ester is hydrolyzed rapidly:⁴⁹⁰



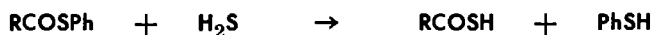
As little as 0.75 mg. of CH_3COS^- may be determined by alkaline hydrolysis and measuring the absorption at 546 m μ after the addition of sodium nitroprusside.^{458a} Phenyl thiolacetate may be analyzed by estimating the thiophenol which is set free.²⁹⁰ Several studies have been made of the kinetics of the hydrolysis.^{405, 500, 534} Phenyl thioacetate is hydrolyzed more slowly than phenyl acetate in acid medium, but in alkaline the rates are about the same.⁷⁴ The acid-catalyzed hydrolysis of ethyl thioacetate is monomolecular, while the alkaline is bimolecular.⁶¹⁵ Methyl and ethyl acetates, on account of lower activation energies, hydrolyze in alkali more rapidly than the corresponding thioesters, but the reverse is true

with the *i*-propyl and *t*-butyl pairs of esters.⁶⁰⁸ A study has been made of the acid and alkaline hydrolysis of a number of thiol-esters.⁵⁷⁹ The alkaline hydrolysis of triphenyl-methyl thiobenzoate proceeds normally with the formation of sodium benzoate and triphenylmethyl mercaptan, but the products from the acid hydrolysis are triphenylcarbinol and thiobenzoic acid.³³⁹

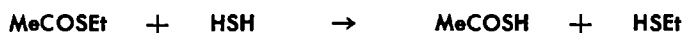
The hydrolysis rates of MeCOSPh_3 and MeCOOCPh_3 have been compared.⁵⁰⁰ Studies on the kinetics of the aminolysis of thiol esters have been made.^{405, 534}

With mercuric acetate, the mercaptide, EtSHgOAc , is formed from ethyl thiolacetate. Sodium chloride changes this to the chloride, EtSHgCl .^{490, 610b}

In the presence of alkali, a phenyl thiol ester is split by hydrogen sulfide:^{731, 734, 735}



In liquid hydrogen sulfide, thiohydrolysis takes place:



The extent of this has been measured for different thiolacetates. At the mole volume of 10 liters the percentages of decomposition are:⁵⁶⁷

Methyl	4.52	<i>n</i> -Propyl	49.3	<i>i</i> -Propyl	30.8
Ethyl	10.10	<i>n</i> -Butyl	68.0		

In transesterification, as in direct esterification, mercaptans function as alcohols, their oxygen analogs. Earlier in this chapter it was shown that when a mixture of equivalent amounts of benzoic acid and ethyl mercaptan, or a similar mixture of ethyl thiobenzoate and water, is heated, equilibrium is reached when there is 14.7% of ester and 85.03% of unchanged benzoic acid, the ratio being 1 to 5.8. As is well known, the esterification limit for benzoic acid and ethyl alcohol is 66.5% of the ester, the ratio here is 2 of ester to 1 of benzoic acid. From these ratios it may be concluded that an equilibrium would be reached in a mixture of equivalent amounts of ethyl benzoate and ethyl mercaptan, or in a similar mixture of ethyl thiolbenzoate and ethyl alcohol, when the concentration of ethyl benzoate is 2×5.8 , or 11.6 times that of the thiolbenzoate (8% to 92%). In a study of the interdependence of limits,^{575a} weighed amounts of ethyl benzoate and

ethyl mercaptans were heated in sealed tubes for 45 hours at 220°. Mixtures of ethyl thiolbenzoate and ethyl alcohol were given the same treatment. Analysis of the resulting mixtures showed that alcoholysis of the thiolester had gone far while mercaptanolysis of the oxygen ester had proceeded only a little way. Equilibrium had not been reached in any of the mixtures, but it was estimated from the figures that had equilibrium been reached it would have been close to that predicted.

Transesterification, like esterification, is catalyzed by a strong acid such as hydrogen chloride; it takes place, however, in the matter of seconds in the presence of a trace of a sodium alcoholate. The methanolysis of thiolesters, many of which can be prepared readily by the addition of thiolacetic acid to an unsaturated, is a convenient method of preparing mercaptans. The thiolacetate is dissolved in four or five equivalents of anhydrous methanol to which has been added about .02% of sodium. Distillation removes the resulting methyl acetate as a binary with the methanol, followed by the excess methanol, leaving the free mercaptan.^{575c} Obviously this method can not be used for mercaptans boiling below 65°.

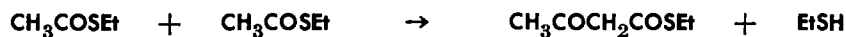
In spite of the unfavorable position of the equilibrium, it should be possible to replace an alcohol by a mercaptan, provided the mercaptan boils sufficiently higher than the alcohol. Thus distillation of a mixture of methyl adipate and an excess of hexyl mercaptan, containing a trace of sodium methylate, should give dihexyl *bis*-thioladipate.

A thiolester reacts with the Grignard reagent, as would any other ester, to form a tertiary alcohol: ³⁰²



Ethyl thiobenzoate and phenyl magnesium bromide give triphenyl carbinol.²⁵⁹

Thiolacetic esters undergo the aceto-acetic ester condensation with sodium ³⁵ or a Grignard reagent: ¹⁵²



Phenyl thiolacetate does not undergo the Fries rearrangement.^{24, 28, 109, 680} The failure of the Fries reaction to occur with any aryl thiol ester is attributed to aromatic deactivation through resonance whereby the sulfur expands its valence shell.⁶⁸⁰

Ethyl thiolacetate and methyl iodide give trimethyl sulfonium iodide. Ethyl iodide reacts similarly.⁵⁵⁰

The ester, $\text{MeCOSCH}_2\text{CO}_2\text{H}$, condenses with cyanacetic ester to $\text{MeCOSCH}_2\text{C}(\text{OH})\text{:C}(\text{CN})\text{CO}_2\text{Et}$.⁴⁹ This may be due to the activating effect of the sulfur atom in the β -position.

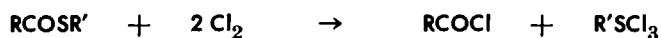
The Reformatsky reaction takes place with α -halogenated thio-carboxylic esters as well as with the oxygen esters.⁵²⁸

Vinyl thiolacetate can be polymerized to a polythiolacetate which can be hydrolyzed to a polyvinylthiol.^{100, 188, 244, 588} The molecular weight of such polymers can be increased by subsequent reaction.²⁰⁸ Thiol acrylic esters can also be polymerized.³⁴⁰

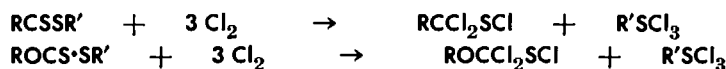
Reduction of thioesters with Raney nickel gives various products according to conditions,²⁶⁷ alcohols,^{263, 503} aldehydes,^{439, 464, 465, 743a, 743b} sulfides, and hydrocarbons.^{294, 295} With lithium hydride the yield of aldehyde is 70% but only a trace with sodium or calcium hydride.⁸⁸ Thioesters of desoxycholic acid with Raney nickel are reduced to cholanal or cholanes.⁶⁶¹

The oxidation of a thioester, $\text{R}'\text{COSCH}_2\text{R}$, by peracetic acid gives the two acids, RCO_2H and $\text{R}'\text{CO}_2\text{H}$, if both R and R' are aromatic, but if either radical is aliphatic, one of the products is the sulfonic acid, $\text{RCH}_2\text{SO}_3\text{H}$.^{45, 614} The thiolsulfonate, $\text{RCH}_2\text{SO}_2\text{SR}$, seems to be an intermediate.¹²⁰ Thioesters of acetic acid have been found to be oxidised by concentrated sulfuric acid to give sulfur dioxide, acetic acid, and the disulfide.²⁴⁴

The chlorination of a thiolacetate may yield the disulfide, RSSR , the thiolsulfonic ester, RSO_2SR , and the sulfone chloride, RSO_2Cl .¹⁸⁴ Chlorination of an aromatic thioester in concentrated sulfuric acid, followed by the addition of aqueous acetic acid, gave the sulfone chloride.⁴⁵⁷ A sulphenyl chloride, RSCl , has been obtained by chlorination in carbon tetrachloride.²³⁶ Extra chlorine is taken up by the sulfur when dry chlorine is passed in at -80° :



One sulfur atom of a dithioester is replaced by chlorine:¹⁸⁵



When titrated with bromate-bromide, a thioester uses up six equivalents of bromide.²⁵³

A thiazole has been prepared from the ester, $\text{MeCOSCH}_2\text{COMe}$ and formamide.⁵²⁵

A thaw melting point diagram has been constructed for the system phenyl benzoate-thiobenzoate.⁵⁸⁵ Eutectics have been determined for a large group of binary mixtures of esters, thioesters, and selenoesters.^{582a, 583, 584} Ultraviolet absorption spectra have been studied.^{135, 372} The infrared spectra and molecular refractivity of some perfluorothiol esters have been compared with those of nonfluorinated esters.²⁹⁷ A new color test for thiols and thioesters is the red color produced when they react with N-ethylmaleimide in an alkaline medium. The advantage claimed is the stabilization of the thiols during chromatography.⁵¹

The Biological Importance of Thioesters

The importance of thioesters in biological processes is gaining increasing recognition. This subject has been ably reviewed by Stadtman.^{664e}

From a study of metabolically active thioesters and their derivatives it has become evident that, due to their reactivity in biosynthetic processes, they play an important role in intermediary metabolism.^{182, 459, 657} Various types of enzymatic reactions have been found to involve the synthesis or utilization of thioesters.^{48, 132, 133, 268, 353.5, 354, 362, 363, 371.5, 408, 409, 446, 447, 458b, 460, 470, 493, 509, 561, 664d, 665, 666, 669.5, 670a, 699, 728}

It has been shown that the hydrolysis of thioesters is accompanied by a large change in free energy, thus placing these compounds in the class of energy-rich substances, which may account for the role they play in energy transfer mechanisms.^{86, 470, 664a, 671} Thioesters have been found to be involved in the oxidation of various aldehydes. An early recognized example of this is the oxidation of methylglyoxal to lactic acid. Although it had been known that this so-called glyoxalase reaction requires the presence of glutathione, its actual significance was much later clarified by Racker.⁵⁶⁰ Recent studies involving the use of certain enzyme preparations have expanded our understanding of the oxidation of various aldehydes to thioesters.^{110, 146, 218, 292, 513, 545, 561, 640, 698, 699} Investigations of the mechanism of α -ketoester acid oxidation have shown that it involves two sulfur-containing enzymes, lipoic acid, and CoASH, the latter a widely distributed

nucleotide derivative that is an important factor in many metabolic processes.^{274, 363, 407, 573}

Two types of thioester interchange reactions are known to be catalyzed by specific enzymes, one of these involves the transfer of the acyl group to other mercaptans,^{85.5, 86, 292, 479, 664a, 664b, 678.5, 729} whereas the other is concerned with the enzymatic transfer of the S-alkyl group to various acids.^{268, 469, 470, 664c, 670b}

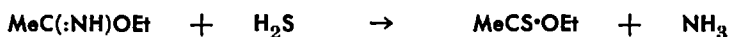
Uses

Ethyl thiolacetate has been recommended as a corrosion inhibitor.¹³⁹ It is fairly toxic to several pests.⁶⁴⁷ The isobutenyl ester, $\text{MeCOSCH}_2\text{CMe:CH}_2$, is claimed as an insecticide.^{5b} Esters of some higher thiolacids have been tested as lubricants.⁵⁶⁴ Other thioesters have been claimed as oil additives.⁴⁰¹ Thioesters may be used to control the polymerization of dienes.⁶⁴⁴ Aromatic esters of dibasic thioacids are said to impart plasticity to rubber.⁶⁵⁰ High molecular weight thioacid esters are said to be useful for moisture-proofing cellophane.¹²⁸

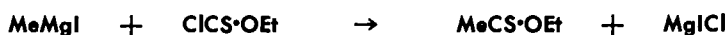
Esters of the type $\text{PhCHRCOSCH}_2\text{CH}_2\text{Net}_2$, in which R is cyclopentyl or cyclopentenyl, are claimed as antispasmodics.⁷⁴⁸ Other thioesters, $\text{RCOSCH}_2\text{CH}_2\text{Net}_2$, in which R is partly cyclic, are said to have therapeutic value.²⁵⁵ Several esters of *p*-aminothiobenzoic acid,^{285, 286, 454} esters, $2,4\text{-RO(H}_2\text{N)C}_6\text{H}_3\text{-COSCH}_2\text{CH}_2\text{NR}'_2$,⁴⁵³ and other thioesters⁴¹⁹ are local anesthetics. Several complex thiolacetates are said to have antispasmodic activity.³²⁹ A study of the tuberculostatic action of thioesters of pyrazinoic acid and other thioesters, many of which are ethyl thioesters, indicates that activity resides in ethyl mercaptan itself.^{420.5} A thioxylene ester of trichloroacetic acid is said to be a pesticide.²⁷⁹ *p*-Cresyl thioacetate and thiochloracetate produce eczema.²⁴ Phenyl esters of aliphatic thioacids, in high dilution, inhibit the growth of fungi.⁴⁹⁵

THIONESTERS, $\text{RCS}\cdot\text{OR}'$

Thionesters have received scant attention. They have been prepared in several ways, most often by the reaction of hydrogen sulfide on an iminoester: ^{286, 359, 411, 478, 482b, 612a, 612b}



Thionesters have been made from the iminoesters derived from α - and β -campholen nitriles.¹⁶ A Grignard reagent reacts with a chlorothioformate: ^{173a, 173b, 173c}



A thionacyl chloride and an alcohol give a thionester: ^{482b, 668}

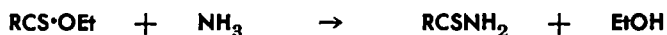


A thionformate is one of the products of the action of phosphorus pentasulfide on an orthoformic ester.^{89, 90} Thiocoumarin from coumarin and phosphorus pentasulfide is a thionlactone.⁶⁸⁸

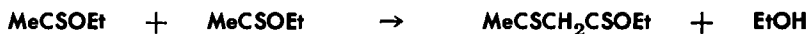
Thionesters, which have appreciable vapor pressures at ordinary temperatures, fume in the air and show phosphorescence.^{173a, 173b} The hydrolysis of a thionester gives hydrogen sulfide and alcohol: ⁸⁹



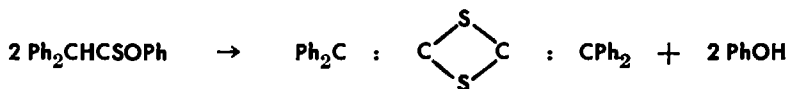
Ammonolysis gives the thioamide: ^{612c}



The Claisen condensation of ethyl thionacetate gives ethyl thioacetothionacetate:



This forms a sodium salt, MeC(SNa):CHCSOEt .⁴¹¹ Chlorination of methyl thionpropionate gives a white, unstable solid.¹⁸⁵ Acetophenone results from the reaction of ethyl thionbenzoate and phenylmagnesium bromide.²⁵⁹ Phenyl diphenylthionacetate gives a cyclic compound at 250°: ⁶³³



Aniline and ethyl dithionoxalate, $\text{EtOCS}\cdot\text{COEt}$, give ethyl thio-carbamate, EtOCSNHPh .

Dithioacids, $\text{RCS}\cdot\text{SH}$

These are also known as carbodithioic acids. Dithioacids are not well known as, on account of their instability, they are not easy to handle. The most general method of preparation has been

the addition of carbon disulfide to a Grignard reagent: 7, 79, 80a, 81, 320a, 321, 322, 391, 655, 691, 754a, 755, 757



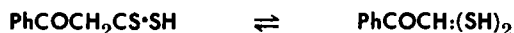
In making dithiobenzoic acid, the carbon disulfide may be added to the mixture of phenyl bromide, ether, and magnesium.^{64a}

Carbon disulfide reacts with the sodium derivative of acetoacetic ester: 199, 520

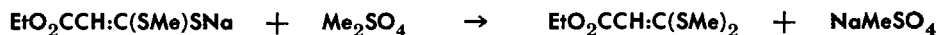


A similar reaction takes place with the sodium derivative of malonic ester.⁴⁸⁶ If bromine is added to the mixture, the product appears to have the trithioanhydride structure, $-\text{CS}\cdot\text{S}\cdot\text{CS}-$.⁷¹⁶ The reaction of carbon disulfide with metal derivatives of hydrocarbons is quite general.⁶³¹ In the presence of sodium, carbon disulfide condenses with compounds containing active hydrogen to form dithioacids. With acetone the product is the *bis*-dithioacid, $\text{OC}(\text{CH}_2\text{CSSH})_2$, which loses hydrogen sulfide to give $\text{SC}:\text{CH}\cdot\text{CO}\cdot\text{CH}:\text{CS}$.^{718a} Another analogous reaction is the formation of sodium cyanodithioformic acid from sodium cyanide and carbon disulfide in dimethyl formamide.³³

When acetophenone, powdered potassium hydroxide, and carbon disulfide are brought together, a small amount of a salt is formed which has been given the structure $\text{PhCOCH}:(\text{SK})_2$. Alkylation of this gives the dialkyl derivative, $\text{PhCOCH}:\text{C}(\text{SR})_2$. The free acid has been given the structure $\text{PhCOCH}:\text{C}(\text{SH})_2$.³⁶⁷ It will be noted that this is isomeric with the dithio acid. It is here suggested that there is tautomerism:



Alkylation of the unsymmetrical malonic ester, $\text{H}_2\text{C}(\text{CO}_2\text{Et})-\text{CS}_2\text{Me}$, with dimethyl sulfate gives the 2,2-*bis*-methylmercaptoacrylic ester, $(\text{MeS})_2\text{C}:\text{CHCO}_2\text{Et}$.⁴²² This may be looked at as the alkylation of the sodium salt of the ester in its tautomeric form;



Trihydroxydithiobenzoic acid is formed by the condensation of potassium xanthate with pyrogallol.⁴⁴⁸ *o*-Hydroxyquinoline reacts similarly.⁴⁴⁹ A thiolactam is formed by the addition of carbon disulfide to methylenepyridines or methylenequinolines.⁶²⁷

Some aromatics react with carbon disulfide, in the presence of aluminum chloride, to give aromatic dithioacids.³⁴⁹ The same is true of antipyrine.⁵⁰ If an alkyl halide is present the product is an ester of the dithioacid.^{50, 349}

Dithioformic acid has been prepared from chloroform and potassium sulfide: ^{438a, 693}



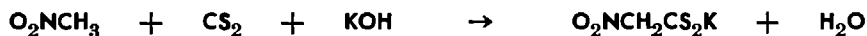
The potassium salt, recrystallized from alcohol, is yellow and melts with decomposition at 193°. The free acid is a colorless solid, insoluble in ordinary solvents, melting at 55–60° with decomposition. Its properties indicate that it is polymeric. Its potassium salt reacts with alkyl halides to give the esters which are trimeric in benzene. There are two forms of the phenyl ester, m. 77° and 154.5°. The potassium salt can be oxidised to the polymeric disulfide, (HCS·SS·CSH)_n. Carbon tetrachloride may be used instead of chloroform.^{438a, 438b} The ethyl ester may be obtained by the reduction of the chloroformic ester ClCS₂Et.^{323b}

One author claims to have gotten sodium dithiopropionate from propionitrile, hydrogen sulfide, and sodium hydrosulfide.¹⁹⁰

Benzotrichloride and potassium sulfide give potassium dithiobenzoate.^{200, 315a} Benzal chloride and potassium hydrosulfide give the same salt along with other products.^{222, 394, 746} The thioaldehyde, the primary product, may have undergone a Cannizzaro reaction.⁷⁴⁶

The result of the reaction of an aromatic aldehyde with hydrogen persulfide ^{66, 67, 309} or with ammonium polysulfide ^{80b, 101a, 102, 727} is a dithioacid or salt. Dithiofuroic acid, C₄H₃O·CS₂H, has been made in this way. It is readily oxidised to the disulfide.^{101b, 434} This is involved in the Willgerodt reaction.

Nitromethane, carbon disulfide, and potassium hydroxide react in alcohol solution:



This salt separates from dilute alcohol as brown crystals which decompose at 203°. The free acid can not be isolated.²³²

Dithioacids are strong acids, and can be titrated sharply. Their odors are nauseous. Even the dithioacetic acid is practically insoluble in water. Its alkali and alkaline earth salts are soluble in water. Copper, silver, lead, mercury, cobalt, nickel,

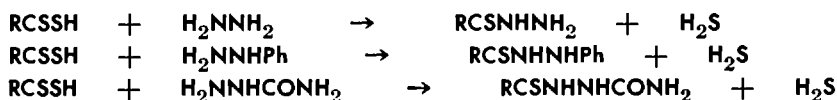
cadmium, ferrous, and ferric salts have been described. Many of them are colored.³²² The blue nickel salt, $(\text{PhCSS})_2\text{Ni}$, m. 219° , takes up sulfur from sodium polysulfide to form a violet salt, m. 195° .³⁰⁴ 2-Methyl-5-*i*-propyldithiobenzoic acid forms colored complexes with heavy metal salts.⁷²² The ammonium salts of the acids may be obtained by passing ammonia into their ether solutions. In nonpolar solvents the free acids have the same optical properties as their esters, indicating the structure $\text{RCS}\cdot\text{SH}$; but in dilute aqueous solutions they resemble their salts:²⁸⁸



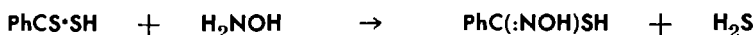
Chromatography has been found to be efficient in the separation of dithioacids. Diastereoisomers were partially separated by this method.^{347, 416}

A dithioacid can be oxidised to the disulfide, $\text{RCS}\cdot\text{S}_2\cdot\text{CSR}$,^{101a, 320a} even by air.³²² The red solution of the α -naphthyl dithiodisulfide in naphthalene at 90° does not obey Beer's law which indicates dissociation into free radicals.⁶²⁸

A dithioacid reacts with an amine to form a thioamide.^{526, 693} This is a general reaction of dithioacids and amino compounds.^{7, 461, 692} Certain amines react with the salts of aryl carbodithioic acids in the presence of oxidising agents to give thioamides.⁶⁵³ With hydrazine,³⁴⁵ phenylhydrazine,^{754a, 754b} or semicarbazide^{655, 754b, 755} the usual elimination of hydrogen sulfide may take place:



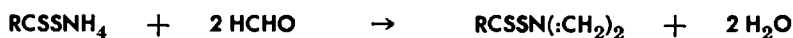
With semicarbazide, particularly, both sulfur atoms are eliminated with the formation of a semicarbazone of the corresponding aldehyde.^{754b} Thus aldehydes may be prepared from dithioacids.^{655, 755} With hydroxylamine, oximes of the corresponding aldehydes or nitriles may result.^{754b, 757} An oxime may be formed:



This may be alkylated or acylated on the sulfur.^{114a}

o-Phenylene diamine cleaves a carbodithioic acid to give a substituted benzimidazole and other products.⁷⁶⁰

By the reaction with formaldehyde the four hydrogen atoms of the ammonium salt are replaced by two methylenes: ^{438c}



The action of thionyl chloride on dithiobenzoic acid is to form the trisulfide, $(\text{PhCSS})_2\text{S}$. With thionyl chloride and chlorine, thiobenzoyl chloride, PhCSCl , is obtained. ^{64a, 668}

Cyanogen chloride and sodium dithiobenzoate form a water-insoluble product. ⁵⁵²

Hexahydrodithiobenzoic acid has been oxidised by nitric acid to the oxygen acid. Its esters have been prepared by alkylating the sodium salt. ⁸¹

Dithioacids effect the *cis* to *trans* isomerization of unsaturated acids. ⁶³⁹

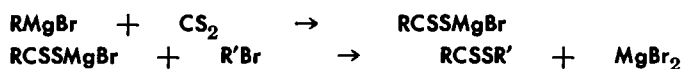
Administering magnesium dithiosalicylate to dogs increased the urinary cystine. ¹⁷⁴

Salts and disulfides of dithioacids can be used as accelerators in vulcanization ¹⁰² or as intermediates in making accelerators. ^{738a} Alkyl esters of *p*-hydroxydithiobenzoic acid may be used in making antioxidants. ⁷⁶³

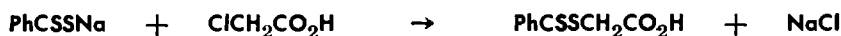
Salts of certain polymeric dithio acids have been used as insecticides, softeners in the lacquer and synthetic resin industry, or as polymerization controllers.

Dithioesters, $\text{RCS}\cdot\text{SR}'$

The esters, $\text{RCS}\cdot\text{SR}'$, can be prepared from the addition products of carbon disulfide to Grignard reagents without isolating the dithioacids: ^{323a, 323b, 391}



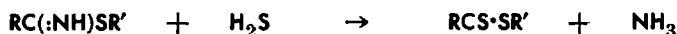
A sodium salt reacts with an alkyl halide: ^{79, 80a, 80b, 315a, 391}



Thiobenzoyl chloride and a mercaptan give a dithioester: ⁶⁶⁸



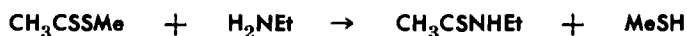
An important general preparation method is the reaction of hydrogen sulfide with thioiminoesters: ^{359, 477, 612a, 612b}



A thioamide can be esterified by a mercaptan: ^{575b}

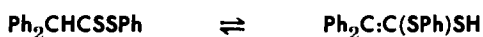


This is the reversal of the reaction of a dithioester with an amine to give the thioamide: ^{149, 391, 612c}



Dithioesters are reddish-yellow oils which are sensitive to oxidation and must be distilled in an inert atmosphere. Some of them give thermochromic solutions. A solution of methyl α -dithionaphthoate in ethyl benzoate is yellow-orange but becomes red-orange on heating.⁶²⁹

One ester appears to be tautomeric:



It gives the Rheinboldt reaction for a mercaptan but fails to do so when heated in an indifferent solvent.^{632, 633} Methyl tetrathio-oxalate, $\text{MeSCS}\cdot\text{CSSMe}$, crystallizes in two forms, m. 71.5° and 101.5° .³⁰⁷ This ester has been obtained by reducing carbon disulfide with sodium and methylating the product.²¹⁷ Two molecules of dithiobutyrolactone condense with the loss of one molecule of hydrogen sulfide. The triclinic crystals melt at 114° .⁶⁸⁹ A sample of ethyl dithioformate became viscous on standing overnight and then could not be distilled even at 0.5 mm.⁸⁹ Ethyl dithiobenzoate and excess of phenylmagnesium bromide give triphenylmethyl thiobenzoate, PhCOSCPH_3 .²⁵⁹

With Raney nickel methyl dithiophenyl acetate is desulfurized to ethylbenzene.³⁰

The absorption spectrum of 2-dimethylaminoethyl dithiobenzoate has been studied.³⁹⁸

Trithio-orthoesters, $\text{RC}(\text{SR}')_3$

The so-called ortho esters and their sulfur analogs are really not esters. They resemble the formals and thioformals in that they are resistant to strong alkali. The only ones that are well known are the orthoformates:



These are to be compared with the formals and thioformals:



The trithio-ortho esters may be made directly from formic acid and a mercaptan: ^{320b, 323c, 613}



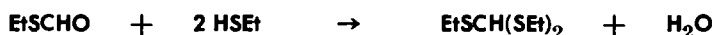
A mercapto-acid reacts similarly: ^{314a, 320b}



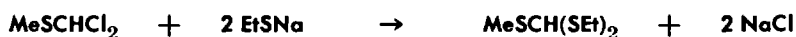
Anhydrous oxalic acid may be substituted for the formic.^{323c} As anhydrous formic acid is not readily available and as water is produced in the reaction, it is advantageous to start with a formic ester:



A mixture of ethyl formate and mercaptan cooled in a freezing mixture and saturated with hydrogen chloride, separates into two layers. The organic layer is taken up in ether and washed with aqueous alkali.^{314b} This method has been used with benzyl ^{323c, 369} and dodecyl ²²⁸ mercaptans. Whether the starting material is formic acid or its ester, the thioformic ester may be regarded as an intermediate. Towards a mercaptan this behaves as an aldehyde:

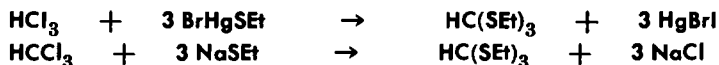


This is substantiated by the fact that mixed trithio-orthoesters can be prepared. A mixed trithio-orthoacetate, $\text{CH}_3\text{C(SEt)-(SCH}_2\text{Ph)}_2$, has been reported.³⁶⁸ A mixed ester has been made from sodium ethyl mercaptide and α,α -dichloromethyl sulfide: ⁷³



Starting with esters of thioacetic, thiopropionic, and thiobenzoic acids the corresponding trithio-orthoesters have been made.³⁶⁸

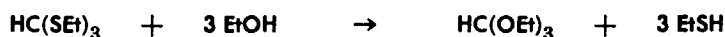
From iodoform and ethylmercaptomercuric bromide, or from chloroform and sodium mercaptide, trithio-orthoformic esters have been obtained: ^{12, 246a}



Carbon tetrachloride reacts with sodium mercaptide, but the product is the trithio-orthoformate ^{29, 177} instead of the tetrathio-orthocarbonate, C(SEt)_4 , as previously was supposed.^{392a} The mechanism of this reaction has been discussed in connection with a study of the alkaline hydrolysis of carbon tetrachloride.³⁰⁸

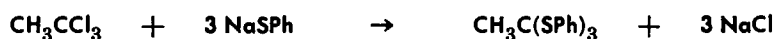
A polymeric ethylene trithio-orthoformate results from the reaction of ethylene mercaptan and triethyl orthoformate.³³¹

An alcohol displaces a mercaptan:



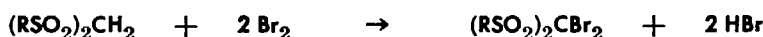
This reaction takes place in the presence of zinc chloride⁴⁹⁶ or of an acid.²⁸²

A trithio-orthoacetate was supposed to be obtained from methylchloroform and a mercaptide:⁴²⁶



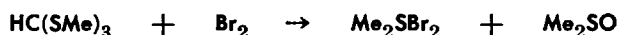
The product of this reaction has been found to be $\text{PhSCH}_2\text{CH}_2\text{-SPh}$, m. 71.5° . The true triphenyl ester, m. 146° , results from the treatment of phenyl thioacetate with boron trifluoride.⁶⁸⁰

The trithio-orthoformic esters are stable in the presence of even concentrated alkali but are hydrolyzed readily by acids. They can be oxidised to disulfides, to sulfonic acids, and to disulfones, $(\text{RSO}_2)_2\text{CH}_2$. These disulfones can be brominated:^{314b}

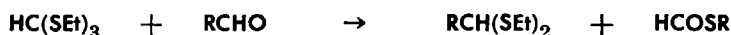


Oxidation in ether solution at a low temperature by perphthalic acid, gives a trisulfone, $\text{HC(SO}_2\text{R)}_3$.⁶¹³ Triphenyl trithio-orthoacetate is oxidised by hydrogen peroxide to benzenesulfonic acid.⁶⁸⁰

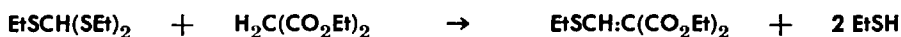
Trithio-orthoesters can be split by bromine:^{323c}



The triethyl ester, HC(SEt)_3 , has been used in the place of the corresponding oxygen compound in the synthesis of carbocyanines³⁷⁶ and for the preparation of mercaptals:^{551a}



With chloral hydrate the product is the hemimercaptal, $\text{Cl}_3\text{CCH(OH)SEt}$.^{551b} When the triethyl ester is heated with malonic ester, acetanhydride, and zinc chloride, two molecules of mercaptan are split out:²⁷³



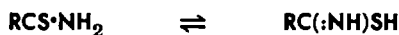
Treating triethyl trithio-orthoformate with phosphorus pentasulfide gives ethyl dithioformate and ethyl tetrathiophosphate.^{89, 90}

The tridodecyl ester has been claimed as a vulcanization accelerator.²²⁸ Orthothioesters and styrene give products useful as oil additives.¹⁴⁸

Triseleno-orthoformate esters have been prepared from selenomercaptans and carbon tetrachloride.⁴¹

Thioamides, RCSNH_2 , RCSNHR' , $\text{RCSNR}'\text{R}''$

Thioamides are tautomeric, having the two structures: ^{104, 423, 717, 737}



Two reviews on thioamides have appeared.^{122d, 432} Thioamides, though formally related to the thioacids, are not prepared from them but are obtained in various indirect ways.

PREPARATION

For preparing thioamides Kekulé's phosphorus pentasulfide method has been used extensively:



This works much better with amides, particularly with N-substituted amides,^{83, 261, 272, 373, 396, 642} than with acids. The yield of thioformanilide, HCSNHPh , is good.^{311e} The thioformanilide is dissolved out of the reaction product by dilute sodium hydroxide and precipitated with acid.⁵¹⁵ Thioformamide has been prepared from formamide and phosphorus pentasulfide.^{248, 311e, 524, 543, 652} The reactants may be brought together in benzene, xylene, ether,^{121, 246b} dioxane^{333c, 721} or tetrahydrofuran.⁶²⁶ Early workers were unable to isolate the pure compound. Powdered phosphorus pentasulfide is added in portions, with cooling, to formamide covered with dry ether. After the mixture has stood for some time and has been shaken for fifteen hours, the thioformamide is dissolved out with water as the hydrate. The water solution is extracted with ether and the ether solution treated with phosphorus pentoxide. Evaporation of this solution gives the pure anhydrous thioformamide.⁷³⁷ Thioacetamide^{287a} and thio-propionamide³²⁶ are prepared in boiling benzene^{287a} or xylene.^{278b}

To prepare thioacetanilide, 54 g. acetanilide, 30 g. phosphorus pentasulfide, and 12 cc. pyridine are mixed and heated on the water bath, with stirring, for 7 minutes. 100 cc. of 25% sodium

hydroxide and 100 cc. of alcohol are added. When solution is effected 100 cc. of water is added, the solution filtered, and carbon dioxide is passed in to precipitate the product.³⁷⁴

Many N-substituted thioacetamides have been prepared similarly.^{341a, 343, 373, 399, 556, 606} This is true also of N-diethylthioacetamide.^{63, 358} Malonanilide is changed to thiomalonanilide, $\text{H}_2\text{C}(\text{CSNHPH})_2$. Methyl succinanilate gives the N-phenylmonothiosuccinimide: ⁵⁷⁹



The phosphorus pentasulfide treatment has been applied to many amides of various kinds.^{55d, 162, 183, 206, 237, 300, 317, 332d, 395, 480, 505a, 505b, 576, 592, 593, 594, 674}

ϵ -Caprolactam gives the corresponding thiolactam.^{412, 554}

The reaction of phosphorus pentasulfide with the oxime of benzophenone gives thiobenzanilide. This may be through a rearrangement of the thio-oxime.¹³⁶

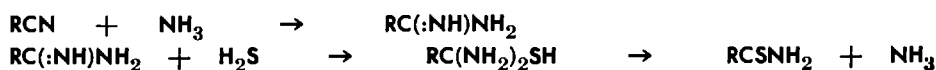
Selenamides may be prepared similarly with the aid of phosphorus pentaselenide.^{183, 332d}

An important method for preparing thioamides is the addition of hydrogen sulfide to a nitrile.^{54b, 97, 112a, 145, 147, 203, 204, 235, 254, 311a, 311b, 360, 377b, 418, 429, 452, 537, 563, 574} At 260° , under pressure, acetonitrile and hydrogen sulfide combine in the presence of a silica-alumina gel.⁴⁶⁸ The rates of addition of hydrogen sulfide to a number of nitriles have been measured.^{377b, 377c} Propionitrile and dry hydrogen sulfide, sealed in a tube, formed crystals in eight days: ²⁵⁴



Similarly cumionitrile unites with hydrogen sulfide.¹⁶¹ The addition takes place particularly well in the presence of ammonia or of an amine.^{39, 54a, 54b, 54c, 55b, 94} An alcoholic solution of the nitrile is saturated with ammonia and then with hydrogen sulfide. The reaction goes on at room temperature, but may be aided by warming.

It seems probable that the ammonia adds first to the nitrile to form an amidine: ^{377a}



It has been shown that hydrogen sulfide can react with an amidine in this way.^{54c, 55c, 702} This explains the fact that an amine may displace ammonia in a thioamide: ^{333c, 489, 624, 705b, 721}

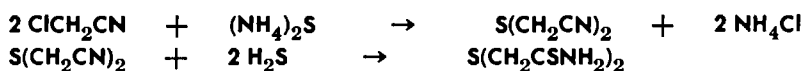


Thioformanilide can be prepared from thioformamide and aniline.⁷²⁰ The higher nitriles are heated with ammonium hydrosulfide in a nonaqueous solvent in an autoclave.^{11, 463, 563, 566} As the ammonia is regenerated only a small proportion of it is required, though a larger amount may be useful in holding the hydrogen sulfide in solution.^{377a} Sodium or potassium hydrosulfides may be substituted for the ammonia.^{205, 350, 428} It is desirable to dissolve an aromatic nitrile in a mixture of pyridine and triethylamine.²¹²

This method of preparation serves for nitriles containing various substituents. Alkoxy-thioamides can be obtained: ^{207, 659}



The hydroxyl group of a cyanhydrin may be protected by acetylation,^{3, 527} though this is not always necessary.^{1a} Thioamides have been made from the cyanhydrins of mesityl oxide and of carvone.^{1a} Carbohydrate nitriles react normally.^{435, 767} Chloroacetonitrile, ClCH_2CN , undergoes a double reaction: ⁷⁶⁹



A nitrile with a less reactive halogen stops at the thioamide: ⁶⁹⁴



3-Cyanomeconin, from opianic acid, gives the thioamide.⁵⁹⁸ Dihydroxytriazinyl-thioformamide is from the corresponding oxime and hydrogen sulfide.⁵³⁰

Polynitriles give the corresponding polythioamides.^{283, 284, 658} When two nitrile groups are on the same carbon atom only one of them may react with hydrogen sulfide.³²⁵

When hydrogen sulfide is added to a nitrile in the presence of an amine the N-substituted thioamide is formed, ammonia being liberated: ^{281b, 377a}

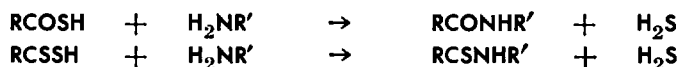


If a dinitrile, $\text{NC(CH}_2)_n\text{CN}$, and a diamine, $\text{H}_2\text{N(CH}_2)_m\text{NH}_2$, in which the amino groups are sufficiently separated, are heated

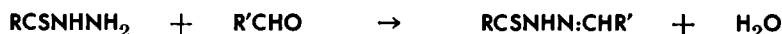
with hydrogen sulfide, a polymer, $[\cdot(\text{CH}_2)_n\text{CSNH}(\text{CH}_2)_m\text{-NHCS}\cdot]_x$ is produced.^{189, 281c} Polymers containing cyano groups may be cross-linked by treating with hydrogen sulfide, or a dimercaptan, in the presence of an amine.⁶⁰² If the amino group in an amino-nitrile, $\text{H}_2\text{N}(\text{CH}_2)_n\text{CN}$, is at the proper distance from the cyan group, ring formation takes place and the product is a thiolactam.^{334, 546} Heating a thiolactam with sodium converts it to a linear polythioamide.¹⁵¹ If the two groups are on the same carbon atom as in amino-acetonitrile, $\text{NH}_2\text{CH}_2\text{CN}$, the six-membered dithioketopiperazine results.^{251, 352} If the amino group is protected by acetylation, cyclization does not take place. Thus $\text{MeCONHCH}_2\text{CN}$ and $\text{MeCON}(\text{Me})\text{CH}_2\text{CN}$ give the thioamides, $\text{MeCONHCH}_2\text{CSNH}_2$ and $\text{MeCON}(\text{Me})\text{CH}_2\text{CSNH}_2$.³⁵³ If the amino group is at a distance as in ω -aminocapronitrile, the product is a linear polymer.¹⁴³

In solution in ether saturated with hydrogen chloride, thioacetic and thiobenzoic acids react with benzonitrile. The final product in both cases is thiobenzamide.^{336b}

Thioacids and dithioacids react with an amine, the one producing an amide and the other a thioamide.^{6, 7, 98, 309.5, 310a, 391, 653, 756, 758a, 759}

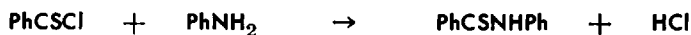


This has been mentioned earlier as a reaction of dithioacetic acid. Hydrazine reacts similarly with a dithioacid or ester. The hydrazides so formed react with aldehydes:^{315e, 345}

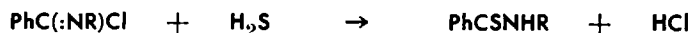


$\text{PhCH}_2\text{CSSCH}_2\text{COOH}$ has been used as a thioacylating agent.³⁹¹

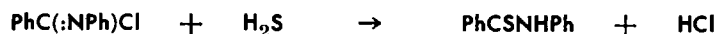
A thioacid chloride and an amine give a thioamide:⁶⁸⁸



The converse of this is the reaction of an acid imido-chloride, with hydrogen sulfide:^{54e, 55e, 433, 708}



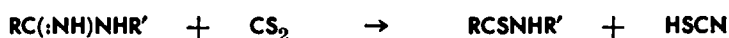
A chloroanilide is converted to a thionanilide:^{705c}



A higher amide, such as lauramide, is converted to the corresponding N,N'-thiodiamide by sulfur monochloride.^{542a}

Heating an amide and hydrated sodium sulfate or an ammonium salt with aluminum sulfide is recommended as a method of preparing thioamides. The sulfuration is effected either by the aluminum sulfide or by the hydrogen sulfide generated by it.^{377c, 380}

An amidine reacts with carbon disulfide: ^{54c, 55c, 57}



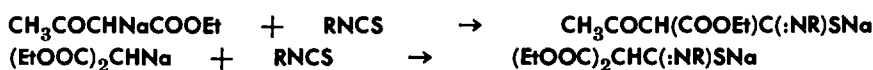
An isocyanide adds hydrogen sulfide on heating: ^{311e, 512}



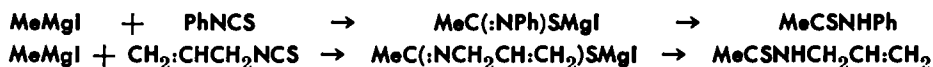
This is reversible; the thioformamide dissociates: ²¹⁰



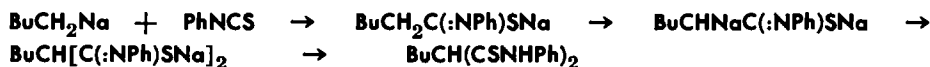
Aniline and chloroform, in alkaline solution, with potassium hydrosulfide give a product containing thioformanilide.^{311e} The isocyanide first formed reacts with the hydrogen sulfide. Mustard oils react with sodium derivatives of malonic ester or acetoacetic ester: ^{486, 749a}



They react similarly with Grignard reagents: ^{75, 609, 749c}



With a sodium alkyl a similar reaction takes place, but the product is metalated by another molecule of the sodium alkyl and then a *bis*-thiomalonanilide is formed: ^{499, 501}

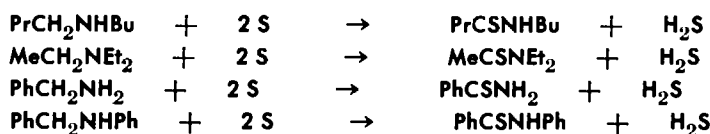


Sodium phenylacetylides and an alkyl or aryl isothiocyanate give a thioamide, PhC:CCSNHR or PhC:CCSNHAr .^{749b, 750, 751} Thiobenzanilide, PhCSNHPh , is from the reaction of phenyllithium on phenyl isothiocyanate.²⁵⁸ N-Arylthiobenzamides are formed from an aryl mustard oil and a phenol, phenol ether,^{252, 481, 591, 696, 723b} or aromatic hydrocarbon²³⁴ in the presence of aluminum chloride.

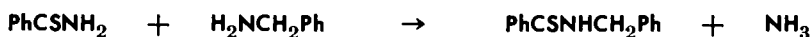
A Schiff's base and sulfur give a thioamide: ⁷⁵



Amines, aliphatic ^{437b} as well as aromatic, ^{466, 705c} can be sulfurized by heating with sulfur at 200°:

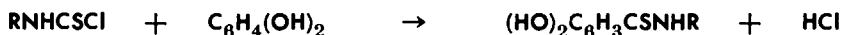


Benzylamine reacts with the thiobenzamide, which is first formed, to give the N-benzylthioamide: ⁴⁶⁶



The N-morpholinothiobenzamide, $\text{PhCSN}(\text{CH}_2\text{CH}_2)_2\text{O}$, is formed from benzylamine, morpholine, and sulfur. ⁴⁶⁶ The reactions are, of course, not as simple as written.

A thiocarbamyl chloride reacts with a polyhydroxybenzene: ³⁶¹



Phenylisothiocyanate reacts with ethyl phenyl sulfide in the presence of aluminum chloride: ²⁵



The dry distillation of a mixture of potassium *p*-toluenesulfonate and potassium cyanide gives some of the thioamide, *p*- $\text{MeC}_6\text{H}_4\text{-CSNH}_2$. ⁶¹⁹

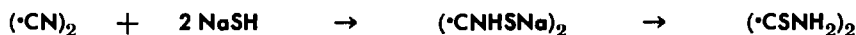
A thioamide is formed from sulfur, ammonia, or an amine with an unsaturate, ^{117, 384b, 437a, 604} an aromatic aldehyde, ^{122b, 123, 278, 332c, 541} or ketone. ^{14, 179, 278, 378c, 381, 382, 385, 473, 514, 599, 636} Thioamides and N-substituted thioamides are intermediates, or final products, in the Willgerodt reaction, ^{119, 384a, 467, 604, 764} for a full discussion of which reference must be made to a review by Carmack and Spielman. ¹¹⁸ Sulfur reacts with a mixture of a methylated heterocyclic and an aromatic amine or aromatic nitrocompound to yield a thioamide. ^{197, 198}

The dithioamide of oxalic acid has received special attention. When cyanogen and hydrogen sulfide are brought together, yellowish red crystals are formed, practically insoluble in water and only slightly soluble in alcohol. The compound was named Rubeanwasserstoff or rubeanic acid. ^{43, 701, 739} It is a monobasic acid, $K = 1.28 \times 10^{-11}$. ⁷⁶¹ It forms heavy metal salts which are decomposed into metal sulfides when boiled with water. ⁵⁶⁸ It is formed from cyanogen dissolved in liquid hydrogen sul-

fide.³⁴⁴ When the cyanogen is in excess the reaction goes only half way:



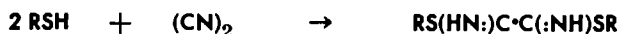
When the two gases are passed into alcohol the nitrile-thioamide, $\text{NC}\cdot\text{CSNH}_2$, called Flaveanwasserstoff or flaveanic acid, separates as beautiful crystals which soon blacken. The black mass is extracted with chloroform from which bright yellow needles are obtained.¹⁰ When dry cyanogen is passed into alcoholic sodium hydrosulfide a salt is formed from which the same compound is precipitated by acid: ^{202, 568, 745}



Its most interesting formation is from cupric cyanide. When ammonium hydroxide is added to a solution of copper nitrate until the precipitate is just dissolved, potassium cyanide added, and hydrogen sulfide passed in, this compound is precipitated.²²⁵ The cyanogen is furnished by the cupric cyanide:



The same compound is obtained from chlorine, potassium cyanide, and ammonium sulfide.²¹⁴ The constitution was determined by Wallach.^{705b} NCCSNH_2 and $(\text{CSNH})_2$ were successfully separated by chromatography.^{674.5} Cyanogen unites with a mercaptan in the presence of a trace of an amine: ⁷⁴⁷



The product is an iminothio-oxamide.

An alkyl oxamide is treated with phosphorus pentachloride and then with hydrogen sulfide. The resulting thioamide can be alkylated: ^{705a, 709}



An oxalic ester-anilide is converted to the corresponding thioanilide by phosphorus pentasulfide: ⁵⁷⁶



An ester nitrile may be converted to a thioamide: ⁷¹³



An unsymmetrical thio-oxamide may be made starting from an oxamide: ^{17, 484}



Dithio-oxalmorpholide, $\text{O}(\text{CH}_2\text{CH}_2)_2\text{NCS}\cdot\text{CSN}(\text{CH}_2\text{CH}_2)_2\text{O}$, is formed in a curious way, by refluxing morpholine with sulfur.³¹⁸ It is obtained also by heating morpholine, sulfur, and an unsaturated hydrocarbon.⁴⁶⁷ It seems likely that thioacetmorpholide, $\text{MeCSN}(\text{CH}_2\text{CH}_2)_2\text{O}$, is an intermediate. This has been gotten by heating morpholine, sulfur, and cyclohexene, in a sealed tube, to 200° ,⁸⁵ and it has been shown that thioacetmorpholide gives dithio-oxalmorpholide when heated with morpholine and sulfur.^{437a}

REACTIONS

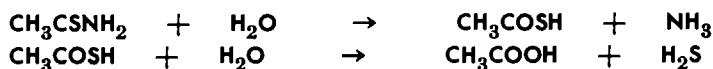
The pyrolysis of a thioamide reverses one mode of its formation.^{54, 566}



This reaction is catalyzed by pyridine.⁵⁶² Distillation of thioacetanilide gives diphenylethenyl amidine.^{341a}

Thioamides give characteristic addition compounds with mercuric chloride ^{55b, 336c, 758b} and platonic chloride.^{420, 544, 569} Thioamides, like their oxygen analogs, are basic enough to form salts when hydrogen chloride is passed into solutions of them in anhydrous, nonpolar solvents. Such salts are hydrolyzed instantly by water.³⁵⁰ Perchloric acid combines with a thioamide in weakly acid aqueous solution, but the product is not simply a salt.⁷¹⁷

Thioamides are hydrolyzed by acids or by bases.^{311e, 415, 576} This must go in two stages: ^{415, 601.5}



A thioamide can be oxidised to an amide.⁸³ At moderate temperatures oxidising and hydrolytic agents convert N-benzyl thioamides to N-benzyl amides; more vigorous treatment cleaves the molecule.⁸³ The sulfur of a thioamide is exchanged for the oxygen of a heavy metal oxide: ^{305, 311c, 433, 570a}



This is the basis for the use of thioamides in analysis to precipitate heavy metal sulfides. With mercuric chloride and ammonia the product is an amidine.^{54a}

In alcohol solution silver nitrate reacts quantitatively with a thioamide: ^{377b}



In alkaline solution the oxidation of the sulfur of a thioamide to the sulfate ion is quantitative and may be used for the estimation of thionsulfur.^{348, 388} In neutral or acid solution the product is RCSONH_2 which may have the tautomeric structure $\text{RC}(\text{:NH})\text{SOH}$.^{388, 390}

Ozone removes hydrogen sulfide from two molecules of thio-benzamide leaving $\text{PhCSNHC}(\text{:NH})\text{Ph}$.³³⁸

Iodine may react in several ways, depending on conditions. It may remove the sulfur as the element ^{570a} or may oxidise a thioamide to the disulfide: ⁷⁵⁸



Or it may cause the formation of a substituted thiadiazole.⁷¹¹ In alkaline solution oxidation to the amide is quantitative.⁷⁴² Oxidation by selenous acid gives the disulfide and selenium.⁷¹⁷

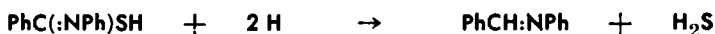
Thionyl chloride and sulfur chlorides may desulfurize thioamides to the corresponding amides or convert them to complicated products.^{129a, 336a, 690}

The oxidation of thioacetnaphthalide to a 2-methylnaphthothiazole involves a hydrogen of the ring.^{341b} The same is true of the oxidation of $\text{PhN:C}(\text{SH})\text{CH}(\text{CO}_2\text{Et})_2$ to a derivative of benzothiazole.⁷⁵²

Nitrous acid converts two molecules of thiobenzamide into a diphenylthiadiazole to which two different structures have been assigned.^{155, 415} Oxidation by a dichloramine takes the same course.^{122a}

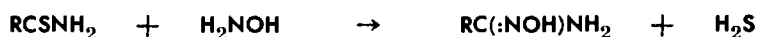
Thioamides can be reduced to primary amines by aluminum amalgam,^{378a, 379, 383} by zinc and hydrochloric acid,^{38, 39, 55b, 161, 311b, 619} or electrolytically.^{377d} Thiobenzanilide is reduced to benzylaniline.⁵⁷ Thiobenzamide is reduced by lithium aluminum hydride to benzonitrile and benzylamine.¹⁵³ Hydrogenation with palladium catalyst gives the amine.⁶⁶⁰ Raney nickel may take a

thioamide to the amine^{96, 410} or all the way to the hydrocarbon.³⁰ Sodium amalgam converts thiobenzamide into trimeric thiobenzaldehyde.^{55b} Stilbene may be produced by zinc and acid.³⁹ Lauronitrile, sulfur, an iron polysulfide catalyst, and hydrogen give lauryl mercaptan. The thioamide must have been formed and then hydrogenated.⁶⁷⁸ A limited reduction to a Schiff's base is possible:¹³⁶



The aldehyde may be obtained by hydrolysis.

A thioamide reacts with hydroxylamine as a ketone would:^{202, 505a, 688}

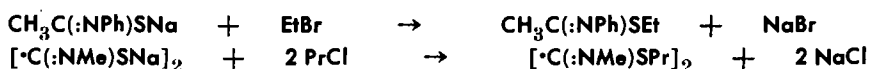


Thio-oxamide gives the dioxime $\text{H}_2\text{NC}(\text{:NOH})\text{C}(\text{:NOH})\text{NH}_2$.²⁰² Isoxazoles can be made from certain thioamide oximes.^{749b, 750, 751}

Thioformanilide, heated with alcohol to 180° in a sealed tube gives a compound, $\text{S}(\text{CH:NPh})_2$, m. 140° .⁵¹⁵ Thio-oxamide condenses with an aldehyde and a secondary base:⁷⁰⁷

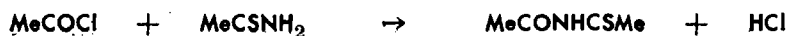


A thioamide dissolves in aqueous sodium hydroxide from which it can be precipitated by carbon dioxide. This is a convenient method of purification. When a concentrated alcoholic solution of a thioamide is mixed with sodium ethylate and ether added the sodium salt is precipitated.^{705d} These sodium salts are very soluble in water and give colored precipitates with heavy metal ions. The sodium salts react readily with alkyl halides: ^{75, 83, 705b, 705d, 706, 710, 758b}

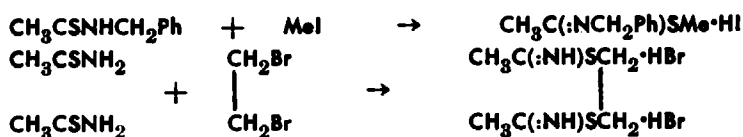


The fact that a mercaptan is obtained by hydrolysis is evidence that the alkyl is attached to the sulfur atom.^{705d} The partial hydrolysis to the ester has been mentioned earlier.

Benzoylthiobenzanilide can be prepared from the sodium salt of thiobenzanilide and benzoyl chloride^{506, 593} and also from the chloride, $\text{PhC}(\text{:NPh})\text{Cl}$, and potassium thiobenzoate.⁵⁰⁶ Acetyl chloride and thioacetamide give the mixed monothiodiacetamide:³⁵⁰

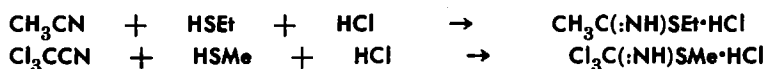


A thioamide may be alkylated also by heating it with an alkyl halide: 55a, 56, 75, 104, 247, 315e, 395, 399, 592, 672, 706, 723a, 737

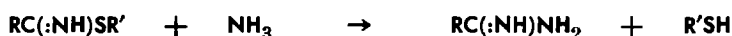


This is analogous to the reaction of an alkyl halide with thiourea which has been given in chapter 1, Volume I as a favorite method for preparing mercaptans. The alkyl halide is supposed to add to the sulfur atom to form a sulfonium complex which rearranges.^{122c, 123, 262} The product is a salt of a thioiminoester from which the free ester is liberated by alkali. These esters form picrates and platinum complexes. On heating, an iminoester salt decomposes into an alkyl halide and a thioamide, reversing the reaction by which it is formed.²⁹¹ The acid hydrolysis to a thio ester has been mentioned above.

The same iminoester salts can be prepared, in an entirely different way, from a nitrile, a mercaptan, and a halogen acid: ^{21, 55a, 171, 172, 332b, 337, 359, 547, 548, 625, 629, 669}



An amine replaces the :NH group of a thioiminoester by :NR.^{172, 580} A thioiminoester and ammonia give an imidine: ^{122c}



A thioamide can be added to a nitrile: ³³⁷



A general method for the preparation of N' thiobenzoylbenzamidines, $\text{PhCSN}=\text{CArNH}_2$, has been described.⁵⁴⁰ Addition of a thioamide to an amidine has been effected.⁴⁸⁸

Resorcinol, an alkyl thiocyanate, and hydrogen chloride give an iminoester hydrochloride, $(\text{HO})_2\text{C}_6\text{H}_3\text{C}(:\text{NH})\text{SR}\cdot\text{HCl}$.³⁶⁴

Thioformamide reacts with proteins to give tough sticky products which contain mercapto groups.⁴⁸⁷

Thioamides condense with halogenated aldehydes, ketones,^{326, 332c, 737} α -haloacids, and various other bifunctional compounds ^{246b, 310b, 570b} to form thiazoles. Examples will be found in the chapter

on thiazoles. This use of thioamides has stimulated their preparation.

α -Aminothioamides condense with ketones and aldehydes to 4-thiohydantoins.^{1b} They can be acetylated, formylated,^{1c} or benzoylated^{1e} by conventional methods. Thiobenzoic hydrazide condenses with chloroacetic acid to a thiadiazole.^{315b} With formaldehyde the product is a thiadiazole.^{758c} α -Aminophenylthioacetamide and diacetyl give 2-acetonyl-2-methyl-5-phenyl-4-imidazolidinethione.^{1c} Derivatives of thiazoline and of thiazolidine may be obtained by the condensation of carboxylic acid thioamides with acetylenecarboxylic acids and their dimethyl esters.⁵⁰⁷

The potassium salt of a thioanilide and an iminochloride give an iminosulfide.⁵⁹³ A thioamide gives colored condensation products with potassium trithiocarbonate,⁶⁸² with $\text{Na}_3\text{Fe}(\text{CN})_5\text{-NH}_2$,⁶³⁵ and with diphenylmethylen chloride, Ph_2CCl_2 .¹³⁴

Thioamides are cryoscopically abnormal, indicating the structure $\text{RCS}\cdot\text{NHR}'$.^{23, 26} In acetamide the freezing point lowering is greater than normal but not so in formamide.¹⁰³

Thioamides form eutectics with their oxygen analogs. Several of these are given in Table 3.1.^{582b}

TABLE 3.1

Eutectics of Amides and Thioamides

<i>Amide</i>	$\text{X}=\text{O}$ <i>M.p.</i> , °C	$\text{X}=\text{S}$ <i>M.p.</i> , °C	<i>Eu</i> <i>M.p.</i> , °C	% <i>Thio</i>
MeCXNHPh	113.6°	75°	49.8°	70
PhCXNH_2	130°	117.4°	80°	56
PhCXNHPh	161°	101.6°	88.5°	82

Thioacetamides in which at least one hydrogen atom remains on the nitrogen are markedly associated.³¹⁷

Thioacetamide forms azeotropes with ethyl sulfide and isobutyl mercaptan.⁴²⁷

The spectroscopic evidence of the structure of thioacetamide is not conclusive but appears to favor the structure, $\text{CH}_3\text{-CSNH}_2$.^{289, 480} The absorption spectrum of thioacetamide is much like that of thioacetpiperidide, $\text{CH}_3\text{CSNC}_5\text{H}_{10}$, which is evidence for the structure CH_3CSNH_2 .^{287b} On the other hand the

molecular susceptibility, 42.45, indicates $\text{CH}_3(\text{:NH})\text{SH}$.^{142b} The Raman spectrum has been studied.¹⁹³ The S-H frequency is missing.^{402, 403} The ultraviolet absorption^{150b, 233} and diamagnetism^{142a} of some thioamides have been determined. The light absorption of C:S is greater than that of C:O.¹⁰⁶ The infrared spectra of the quaternary methiodides of several N,N-disubstituted thioamides have been recorded.²⁶⁶ Certain gold complexes of thioacetamide have been x-rayed.²⁵⁷ Thiobenzamide shows strong and selective absorption. Its mercury salt is a thiol derivative.²⁸⁹

Crystallographic data have been given for thioacetanilide.⁶⁹ Crystals of dithio-oxamide are triclinic.^{449.5}

Thioformamide^{248, 249, 508} and thioacetamide^{40, 68, 219, 220, 221, 430, 445, 649, 712} are superior to hydrogen sulfide for precipitating the sulfides of heavy metals in quantitative and qualitative analysis.

Dithio-oxamide, known as rubeanic acid, is used as a sensitive test for zinc, cadmium, nickel, cobalt, lead,^{472, 703} and especially for copper ions.^{27, 60, 431, 440.5, 472, 590, 603, 736, 740, 741, 753} It has been recommended for the potentiometric titration of copper. Accurate results are claimed.⁴⁸³ In alkaline solution it gives an unstable blue compound with the ferric ion.²⁷ It is employed in a test for the passivity of iron.⁵¹⁶ It gives precipitates with platinum, gold, and chromium ions.²⁷ The ruthenium compound has been studied spectrophotometrically.⁷⁶¹ The solubilities of the copper, nickel, and cobalt salts have been determined in various solvents.⁴⁷² Diphenyl rubeanic acid gives colored precipitates with nickel, copper, cobalt, silver, mercury, lead, bismuth, and gold.^{760.5} Oxanilic thioamide, PhNHCO-CSNH_2 , gives characteristic colored precipitates with metals of the sulfide group.⁴⁷¹ Thiobenzohydrazide and derivatives, PhCSNHNHR , give complexes with nickel.³⁴⁶ The nickel and copper derivatives of dithio-oxamide are used as molecularly oriented dichroic stains in a plastic.⁹

Resinous products are said to be obtained by condensing certain thioamides with formaldehyde.^{93, 163, 328, 332a} Thioamides have been suggested as vulcanization accelerators, insecticides, and fungicides,^{115, 131, 178, 209, 250, 260, 284, 319, 333a, 333b, 497, 511, 563} as corrosion inhibitors,^{44, 283, 284, 442} as additions to lubricating oils,^{284, 563} for textile assistants,¹⁸⁹ and as artificial fibers.⁶⁵⁸ In the copper-catalyzed autoxidation of cyclohexene, the rate decreases when N,N'-dicyclohexyldithio-oxamide is used as the che-

lating agent, but in the iron catalyzed reaction, it is increased greatly.¹²⁷

PHYSIOLOGICAL

Thioacetamide is one of a number of compounds that activate glucolysis in certain bacteria.¹²⁴ It stimulates the germination of dormant lettuce seed.⁶⁸⁷ Several thiohydrazides and thiohydrazones have bactericidal and fungicidal activity.³⁴⁵ Hypnotic effects have been observed in several thioamides.¹²⁹ The hypnotic power of N-diethylthioacetamide is about five times that of acetamide.⁶³ Thioamides have shown antipyretic effects.¹²⁹ Certain thioacetamides produced cancer of the bile ducts in rats,²⁷⁵ while others showed antitubercle bacteria activity.^{271, 404, 444}

Physical Properties of Some Thioacids and Derivatives

The aim is to show what compounds have been made, some of their properties, and who made them. No claim is made for completeness. As has been pointed out in the introductions to similar lists in previous volumes, our knowledge of the properties of the majority of organic compounds is sketchy and often of doubtful accuracy. Divergent data are often given by different authors for the properties of the same compound. Distillation temperatures commonly masquerade as boiling points. Those given for low pressures are especially unreliable.

TABLE 4.1

Elevation of Boiling Points by Acetylation

	<i>ROH</i> <i>B.p., °C</i>	<i>ROAc</i> <i>B.p., °C</i>	<i>Eleva-</i> <i>tion</i> <i>°C</i>	<i>RSH</i> <i>B.p., °C</i>	<i>RSAc</i> <i>B.p., °C</i>	<i>Eleva-</i> <i>tion</i> <i>°C</i>
Methyl	64.5	57.2	-7.3	7.6	98	90
Ethyl	78.32	77.15	-1.17	34.7	116.4	81.7
Propyl	97.17	101.6	4.4	68	139.8	71.8
Butyl	7117.7	126.5	8.8	98	163.4	65.4
Amyl	137.9	148.8	10.9	126.5	185.1	58.6
Hexyl	156.5	169.2	12.7	151.5	205.8	54.3
Heptyl	176.35	191.5	15.2	176.2	227.4	51.2
Octyl	194.7	210	15.3	199.1	247.0	47.9

In Table 4.1, the elevation of the boiling points of alcohols and of mercaptans by acetylation are contrasted. On account of association, the boiling points of the alcohols are abnormally high. Methyl and ethyl acetates actually boil lower than the corresponding alcohols. All of the thiolacetates boil much higher than the mercaptans from which they are derived. The difference decreases from 90° for the methyl to 48° for the octyl.

TABLE 5.1

Boiling Points of Acetates, Thiolacetates, and Thionacetates

	CH_3COOR B.p., °C	Differ- ence °C	$CH_3CO\cdot SR$ B.p., °C	Differ- ence °C	$CH_3CS\cdot OR$ B.p., °C
Methyl	57.2	40.8	98	-10	88
Ethyl	77.15	39.2	116.4	- 6.4	110
Propyl	101.6	38.2	139.8	-11.8	128
Butyl	126.5	36.9	163.4	-16.4	147
Amyl	148.8	36.3	185.1	—	—
Hexyl	169.2	36.6	205.8	—	—
Heptyl	191.5	35.9	227.4	—	—
Octyl	210	37.0	247.0	—	—

In Table 5.1 the boiling points of the thiolacetates and thionacetates are contrasted with those of the acetates. The same is done with the densities in Table 6.1.

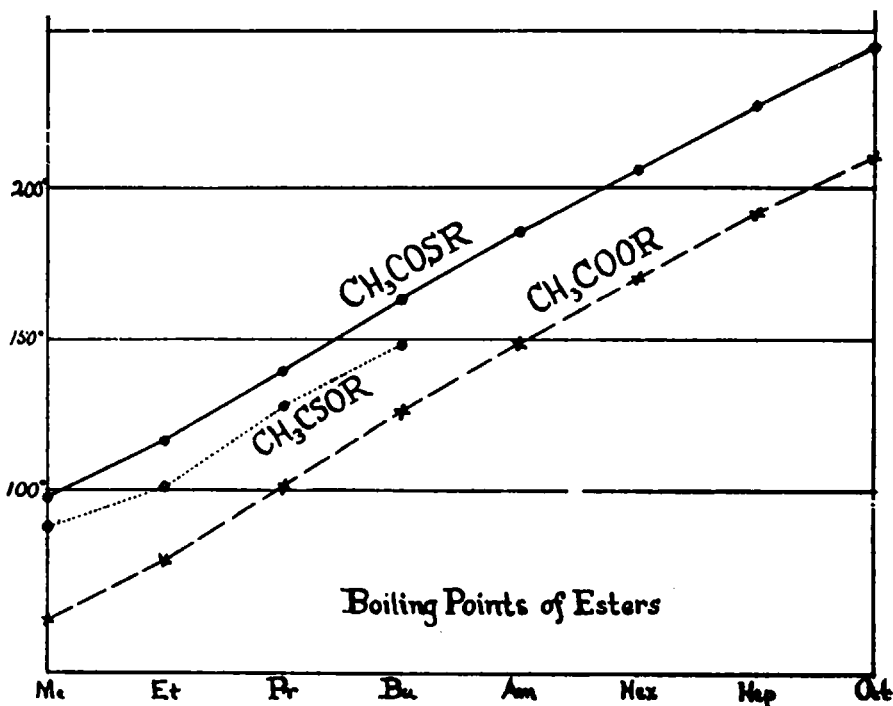
TABLE 6.1

Densities 25/4 of Acetates, Thiolacetates, and Thionacetates

	CH_3COOR	Differ- ence	$CH_3CO\cdot SR$	Differ- ence	$CH_3CS\cdot OR$
Methyl	0.9274	0.0896	1.0170	-0.0372	0.9798
Ethyl	0.8945	0.0794	0.9739	-0.0184	0.9555
Propyl	0.8845	0.0692	0.9537	-0.0552	0.8985
Butyl	0.8761	0.0629	0.9390	-0.0465	0.8925
Amyl	0.8659	0.0626	0.9285	-0.0667	0.8618

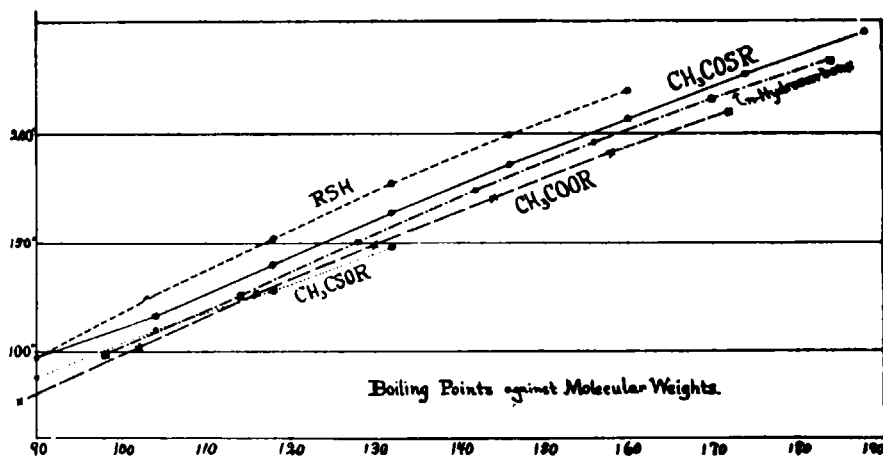
In Figure 1.1 the boiling points are plotted against the number of carbons in the alkyl. In all three series the methyl esters boil

slightly higher than would be expected. The difference between the thiolacetates and the acetates starts at 40.8° with the methyl esters and comes down to about 36.5° at the butyl and then remains approximately constant. The thionesters boil about 10°



lower than the thioesters, but the data are not consistent enough for a close comparison.

In Figure 2.1 the boiling points of the same esters are plotted against their molecular weights. For comparison, the boiling points of the mercaptans and the normal hydrocarbons are added.



The thiolacetates boil slightly above the hydrocarbons and the acetates a little below. The mercaptans are considerably higher.

The differences of the densities of acetates and thiolacetates decrease regularly as the alkyls lengthen. The thionesters have lower densities than the thiol.

The data for dithioesters are too scanty for comparisons.

THIOLACIDS, RCO·SH

- MeCOSH, m. -75° ; b_{760} 87.5° ,¹⁵⁶ b. 93° ,^{13, 173a, 173b, 595, 697} $88-91^{\circ}$,^{138, 590.5} $88-9^{\circ}$,⁴⁶ $85-90^{\circ}$,⁵⁰⁰ $85.5-7.5^{\circ}$,^{196a} 87° ,¹⁹⁵ $97-9^{\circ}$,^{704a} 87.1° ,⁶⁵¹ $85-8^{\circ}$,⁴⁴² $92-7^{\circ}$; ⁶²⁰ d 20/4 1.0693,¹⁵⁶ d_{10} 1.074,^{173a, 697} d_{20} 1.0681; ⁶⁵¹ n 20/D 1.4636,¹⁵⁶ 1.4648,⁶⁵¹ 1.4582,⁴⁶² n 18.8/D 1.4451; ⁴⁶ $K = 4.7 \times 10^{-4}$.²⁸⁸
- EtCOSH, b. $108-9^{\circ}$,^{47, 231} 142° .⁷¹⁴
- PrCOSH, b. $119-20^{\circ}$,²³¹ $125-32^{\circ}$.⁴⁷
- i*-PrCOSH, b. 130° .⁶⁹⁷
- BuCOSH, b. $133-40^{\circ}$.²³¹
- i*-BuCOSH, b. 121° .²³¹
- t*-BuCOSH, b. $125-7^{\circ}$.²³¹
- AmCOSH, b_{65} $98-101^{\circ}$.²³¹
- PrCHMeCOSH, $D-b_{23}$ $71-2^{\circ}$; $[\alpha]$ 25/D 7.49° ; $L-[\alpha]$ 25/D -7.08 .⁴³⁶
- HexCOSH, b_{11} 81° .²³¹
- Me₃CCH₂CH₂COSH, b. $200-15^{\circ}$.⁶⁶²
- HepCOSH, b_{10} 95° ,²³¹ b_3 72° .^{590.5}
- OctCOSH, b_{10} 105° .²³¹
- C₁₃H₂₇COSH, m. 25° .¹⁹
- C₁₅H₃₁COSH, m. 71° .¹⁹
- C₁₇H₃₅COSH, m. $29-51^{\circ}$.^{590.5}
- H₂C:CH(CH₂)₈COSH, polymeric, m. 95° .⁴¹⁴
- PhCOSH, m. 24° ,^{201, 243, 494, 590.5} 18° ; ⁴¹⁴ b_3 75° ,^{590.5} b_{25} $100-12^{\circ}$; ⁴⁷ n 20/D 1.6030.²⁹⁹
- MeC₆H₄COSH, *o*, b_{35} 133° ; ⁶¹¹ *p*, m. 44° ; ^{611, 714} b_{15} 131° .⁶¹¹
- ClCH₂COSH, b_{16} 46° .¹³
- Cl₂CHCOSH, b_{15} 56° .¹⁶⁰
- Cl₃CCOSH, b_{11} 57° ,¹⁶⁰ b_{12} 56° .^{590.5}
- o*-HOC₆H₄COSH, m. 33° .^{590.5}
- p*-FC₆H₄COSH, m. 36° .²²⁶
- p*-BrC₆H₄COSH, m. 78.5° .^{590.5}
- p*-NO₂C₆H₄COSH, m. $90-5^{\circ}$,^{371, 421} 94° .^{590.5}

3,5-(NO₂)₂C₆H₃COSH, dec.^{590.5}
p-PhC₆H₄COSH, m. 92°.¹⁵⁴
 β -C₁₀H₇COSH, m. 48°.^{590.5}
 Ph₂CHCOSH, m. 55°.⁶⁸⁵
 1-PhC₅H₈COSH, m. 44°; K salt m. 167°.⁴⁴¹
 PhCONHCH₂COSH, m. 100°.¹⁵⁴
 H₂NCHMeCOSH, m. 250–5°,⁷³⁴ NBz., m. 94°.⁷³⁵
 C₄H₃O·COSH, m. –9°; b₁₈ 101–3°; n 24/D 1.589.⁵³⁸
 3-C₅H₄N·COSH, thionicotinic, m. 147°.⁷⁰

DIBASIC ACIDS

Thiomalonic, m. 10°.⁶⁷⁵
 Thiosuccinic, m. 27°.^{590.5}
 Monothiosuccinic, m. 61°.^{414, 475b}
 Thioglutaric, m. 10°.⁶⁷⁵
 Monothioglutaric, m. 31°.^{414, 475b}
 Thioadipic, m. 27.5°,^{675, 676} 25°,⁴⁷⁴ 26.5°,^{475a} 24°.^{590.5}
 Monothioadipic, m. 41°.^{414, 475b}
 Thiopimelic, m. 5°,⁴⁷⁴ 13.5°;^{414, 475a} d 20/4 1.158; n 20/D 1.5295.⁴⁷⁴
 Thiosuberic, m. 20–5°,⁴⁷⁴ 16°,⁶⁷⁵ 15.5°.^{414, 475a}
 Thiozelaic, m. 20–5°,⁴⁷⁴ 16°,⁶⁷⁵ 23°.^{475a}
 Thiosebacic, m. 30–5°,⁴⁷⁴ 26°,⁶⁷⁵ 30.5°.^{475a}
 Thioisophthalic, m. 67–73°.⁴⁷⁴
 Thioterephthalic, m. 125–8°.⁴⁷⁴
 2,5-Dimethoxythioterephthalic, m. 139°.^{414, 475a}
 Thiohomoterephthalic, m. 49°.^{414, 475a}
p-Thiophenylenediacetic, m. 73.5°.^{414, 475a}
 1,2,3,4-Tetrahydrothiophthalic, α -b₇ 142–3°; β -b₆ 148–50°.⁶⁴³
 Hexahydrothioterephthalic, *cis*-, m. 38°; *trans*-, m. 80.5°.^{414, 475a, 475b}
 [CH₂CH₂CH₂SCO(CH₂)₄COSH]₂, m. 45°.^{475b}

SELENO-ACIDS

PhCOSeH, m. 133°.⁴⁴³

ACYL SULFIDES, DISULFIDES, AND POLYSULFIDES

(MeCO)₂S, b. 152–4°,^{158b} b₂₀ 62°, b₅₀ 82°,¹⁵⁶ b₂₀ 62–3°,⁷⁷ 66–7°, b₇₄₇ 156–8°,¹⁶⁶ b₇₆₀ 152–4°,^{158b} b. 155–8°,^{77, 130, 169} 157°,^{173b, 173c}

119–20°, ^{681c} 121°; ³⁴³, ^{365a}, ³⁶⁶, ⁶¹⁴ d 20/4 1.1317,¹⁵⁶ 1.122;⁷⁷
 n 20/D 1.4826,¹⁵⁶ n 21/D 1.4810.⁷⁷
 (ClCH₂CO)₂S, m. 47°; b₁₁ 130°. ¹³
 (PhCO)₂S, m. 48°. ², ²⁴³
 (1-PhC₅H₈CO)₂S, m. 114°. ⁴⁴¹
 (Ph₂CHCO)₂S, m. 140°. ⁶⁸⁵
 (MeCO)₂S₂, m. 20°, ³⁶⁶ 21°; ⁴⁵, ⁷² b₁₈ 105–6°. ⁷²
 (BuCO)₂S₂, m. 90°. ^{91a}
 MeCOSSCOPh, m. 50°. ^{74.5}
 (PhCO)₂S₂, m. 130° ², ²²⁷, ⁷¹⁴ 129°, ⁶⁴⁶ 136°, ⁶⁵ 128.5°. ^{46.3}
 (1-PhC₅H₈CO)₂S₂, m. 83.5°. ⁴⁴¹
 (*p*-MeC₆H₄CO)₂S₂, m. 116°. ⁷¹⁴
 (*p*-NO₂C₆H₄CO)₂S₂, m. 183°, ⁶⁵, ³⁷¹, ⁴²¹ 181°. ²⁴⁵
 (3-C₅H₄N-CO)₂S₂, thionicotinic, m. 89°. ⁷⁰
 (MeCO)₂S₃, m. –25°, ^{74.5} –19–7°; d 22/4 1.3423,⁶⁵ d₂₀ 1.3504;
 n 20/D 1.6000; MR 46.2. ^{74.5}
 (PhCO)₂S₃, m. 168°. ⁶⁵
 (MeCO)₂S₄, n 20/D 1.6428. ^{74.5}
 (PhCO)₂S₄, m. 84°, ⁶⁵ 85°. ⁷²
 MeCOSCl, b₁₈ 42°. ⁷¹, ⁷²
 MeCOS₂Cl, b₁ 38–9°. ⁷²

THIOLESTERS

Thiolformates, HCOSR

Ethyl, b₇₆₀ 103–6°; d 25/4 1.019; n 26/D 1.4500. ^{551a}
 Propyl, b₇₅₃ 108.5°; d 23.5/4 0.9323; n 23/D 1.4580. ^{551a}
 Benzyl, b₂₆ 109–11°. ³²⁴

Thiolacetates, MeCOSR

Methyl, b₇₆₀ 98°, ⁷¹⁵ 96°, ³⁰¹ 95–6°, ⁵²², ⁵⁶⁷, ⁶⁰⁸, ⁷⁰⁶ 95°, ^{173b}, ^{173c} 97.5–
 8.8, ^{176.5} 62–8°, ^{112b} b₇₅₂ 95–6°; ⁷⁴⁴ d 0/4 1.0461, d 25/4 1.0170, ⁷¹⁵
 d₃₀ 1.013, ^{186.5} d 30/4 1.0111; ⁶⁰⁸ n 25/D 1.4600, ⁷¹⁵ 1.4620, ⁷⁴⁴
 n 23.5/D 1.4661; ⁶⁰⁸ n 30/D 1.4972; MR_D 24.30. ^{186.5}
 Ethyl, b₇₆₀ 116.4°, ⁷¹⁵ 117°, ⁴⁵⁶, ⁶¹⁴ 116–8°, ⁶⁴¹ 116–7°, ³⁵, ¹⁸⁶ 116°, ³⁰¹
 115–6°, ⁵⁶⁷ 115–7°, ⁷⁰⁶ 114°, ²⁹⁸ 114–6°, ⁴⁹⁰ 113–4.5°, ^{186.5} b₇₃₅
 113.5°, ⁶¹⁵ b₇₄₄ 115–6°; ⁷⁴⁴ d 0/4 1.006, ⁷¹⁵ 1.008, ³⁵ d 20/4
 0.9742, ⁶¹⁵ d 25/4 0.9739, ⁷¹⁵ 0.9740, ⁷⁴⁴ 0.9755, ³⁵ d₃₀ 0.971; ^{186.5}
 n 20.6/D 1.4583, ⁶¹⁵ n 25/D 1.4540, ⁷¹⁵ 1.4564, ²⁹⁸ n 28/D

- 1.4503,³⁵ n 30/D 1.4473; MR_D 28.30; ^{186.5} magnetic susceptibility 0.6019.²¹⁶
- Propyl, b_{760} 139.8°,⁷¹⁵ b_{750} 135°,⁷⁴⁴ $b.$ 137°,³⁰¹ 135–7°,^{567, 706} 137–9.5°; ^{186.5} d 0/4 0.9789, d 25/4 0.9537,⁷¹⁵ 0.9660,⁷⁴⁴ d_{30} 0.955; ^{186.5} n 25/D 1.4558,⁷¹⁵ 1.4540,⁷⁴⁴ n 30/D 1.4533; MR_D 33.6.^{136.5}
- i*-Propyl, $b.$ 122–3°,⁵⁶⁷ 126°,³⁰¹ 124–7°,⁷⁰⁶ 126–7°,⁶⁰⁸ 124–5°,^{186.5} b_{750} 124–6°; ⁷⁴⁴ d_{30} 0.952,^{186.5} d 30/4 0.9322; n 23.5/D 1.4502,⁶⁰⁸ n 30/D 1.4445; MR_D 33.2.^{186.5}
- Butyl, b_{760} 163.4°,⁷¹⁵ $b.$ 134–5°,⁵⁶⁷ b_{738} 159–60°; ⁵¹⁹ d 0/4 0.9628, d 20/4 0.9390; n 25/D 1.4570.⁷¹⁵
- s*-Butyl, $b.$ 148–51.5°; d_{30} 0.933; n 30/D 1.4528; MR_D 38.25.^{186.5}
- i*-Butyl, b_{744} 151–2°,³³⁵ b_{760} 151–2°,⁶⁰⁸ $b.$ 148–50°,⁷⁰⁶ 148°,^{301, 744} b_{737} 149–50°; ⁵¹⁹ d 30/4 0.9291; n 23.5/D 1.4555.⁶⁰⁸
- t*-Butyl, $b.$ 130–3°,^{186.5} 129–35°,¹⁵⁷ 120–30°,³⁰⁶ b_{11} 31–2°,⁵⁸⁶ b_{14} 38°,⁶⁰⁸ b_{28} 44–5°; ⁵¹⁹ d_{30} 0.918,^{186.5} d 30/4 0.9290; ⁶⁰⁸ n 20/D 1.4500,³⁰⁶ n 23.5/D 1.4490,⁶⁰⁸ n 30/D 1.4435; MR_D 38.4.^{186.5}
- Amyl, b_{760} 185.1°,⁷¹⁵ b_{14} 70–1°; ⁵¹⁹ d 0/4 0.9511, d 25/4 0.9285; n 20/D 1.4579.⁷¹⁵
- i*-Amyl, b_{748} 175–7°,³³⁵ b_{737} 174–5°; ⁵¹⁹ d 20/4 0.9256; n 20/D 1.4590.³³⁵
- Hexyl, b_{760} 205.8°,⁷¹⁵ b_{13} 28–9°; ⁵¹⁹ d 0/4 0.9408, d 25/4 0.9192; n 25/D 1.4591.⁷¹⁵
- i*-Hexyl, b_{16} 89°; n 25/D 1.4575.³⁰³
- 2-Methylpentyl-3, b_{13} 70°; n 25/D 1.4603.³⁰³
- Heptyl, b_{760} 227.4°; d 0/4 0.9334, d 25/4 0.9128; n 25/D 1.4600.⁷¹⁵
- Octyl, b_{760} 247°,⁷¹⁵ b_{25} 132–3°,⁹⁹ b_{13} 114–5°; ⁵¹⁹ d 0/4 0.9259, d 25/4 0.9058; ⁷¹⁵ n 20/D 1.4648,⁹⁹ n 25/D 1.4609.⁷¹⁵
- Nonyl, b_{13} 128–9°.⁵¹⁹
- Decyl, b_{13} 140–1°.⁵¹⁹
- Dodecyl, b_1 162–5°; d 20/4 0.891; n 20/D 1.4648.²²⁸
- t*-Dodecyl, b_3 85–95°; n 20/D 1.4785.³⁰⁶
- Cetyl, $m.$ 30.3°; $b_{1.5}$ 168°.⁹⁹
- Cyclohexyl, b_{14} 90°,¹⁶⁰ b_{18} 98°.^{590.5}
- 2-Methylcyclopentyl, b_{25} 101°; n 25/D 1.4900.³⁰³
- 2-Methylcyclohexyl, b_{14} 110°.^{160, 303}
- Vinyl $b.$ 121°; d 25/4 1.0136; n 25/D 1.4892.^{100, 188}
- Allyl, b_{29} 53–4°; d 25/4 0.9850; n 25/D 1.4797.⁵⁰⁰
- 2-Butenyl, b_{25} 73°; d_{20} 0.9811; n 20/D 1.4868.¹⁵⁹

- Hexenyl, b_{20} 83° ; n 20/D 1.4899.³²
 Hexa-1,3-dienyl, $b_{0.001}$ 66° ; n 28.5/D 1.5330.³¹
 Phenyl, m . 19.5° ; ⁶⁸⁰ b . 228° , ^{173b}, ^{173c} $228-30^\circ$, ⁴⁹⁰ $b_{1.5}$ 66° , b_3 82° , ⁶⁸⁰ b_7 95° , ⁴⁹⁵ b_8 $110-1^\circ$, ⁵⁶⁷ b_{11} 110° ; ⁷⁴ n 20/D 1.5700.⁶⁸⁰
 PhCH₂-, b_{10} 120° , ⁴⁹⁵ $b_{0.7}$ $75.5-6.8^\circ$; n 25/D 1.5565.⁵⁰⁰
 PhCHMe-, b_4 105° , ⁹⁹ b_{13} $123-5^\circ$; d 20/4 1.0698; n 20/D 1.5480,^{314c} 1.5429.⁹⁹
 PhCH₂CH₂-, b_{13} $134-5^\circ$; d 20/4 1.0730; n 20/D 1.5428.^{314c}
m-MeC₆H₄-, $b_{1.6}$ $81-2^\circ$; n 25/D 1.5609.⁶⁸⁰
p-MeC₆H₄-, b_{14} 121° ; ²⁴ b_5 100° .⁴⁹⁵
m-MeOC₆H₄-, b_5 119° ; n 20/D 1.5701.⁶⁸⁰
p-MeOC₆H₄-, m . 100° .⁶⁷⁷
 2,4,6-(MeO)₃C₆H₂CHPh-, m . 137° .³⁷⁰
p-EtOC₆H₄-, m . 40° .⁶⁷⁷
p-BrC₆H₄-, m . 52° .⁶⁸⁰
 PhCH:CH-, m . 460° , ^{315c} b_{127} 125° ; n 20/D 1.5475.^{46.5}
 Ph₃C-, m . 147.5° .⁵⁰⁰
 ClCH₂CH₂-, b_{17} $76-6.5^\circ$; d 20/4 1.2010.¹⁶⁸
 FCH₂CH₂-, b_{100} 87° ; d 25/4 1.4041; n 25/D 1.4525.^{196b}
 HOCH₂CH₂-, b_8 95° ; ⁵²¹ Ac., b_{17} $107-8^\circ$, ¹⁰⁰, ¹⁸⁸ b_{25} $118-20^\circ$.⁶⁰⁰
 AcOCH₂CH₂Et-, b_{12} $108-10^\circ$; n 20/D 1.4698.^{46.5}
 CH₃CH(OAc)CHMe-, b_{12} $105-6^\circ$; n 18/D 1.467.^{46.5}
 AcOCH₂CH(C₅H₁₁)-, b_2 122° ; n 20/D 1.4682.^{46.5}
 3-Hydroxy-1-hexenyl, $b_{0.0005}$ 76° ; n 16/D 1.5730.³¹
 3-Hydroxy-3-phenyl-1-propenyl, $b_{0.001}$ 115° ; n 20/D 1.5730.³¹
 AcOCH(CH₂)₄CH-, *cis* b_{12} $134-5^\circ$; n 20/D 1.496; *trans* b_{12} $128-34^\circ$; n 20/D 1.484.^{46.5}
 ClCH₂CH(OH)CH₂-, $b_{0.4}$ 94° .⁶⁵¹
 HSCH₂CH₂-, b_{40} $95-7^\circ$; ⁵⁷¹ diAc., m . $68-73^\circ$, ^{196b} 60° .⁵⁷¹
 HSCH₂CH₂CH₂-, b_{40} $115-6^\circ$; diAc., b_{50} 178° , b_{760} 255° .⁵⁷¹
 MeCOCH₂-, b_2 $130-4^\circ$.⁵²⁵
 MeCOCH₂CH₂CH(CHMe₂)-, b_{10} 134° .⁴²
 MeOCH₂-, b_{15} 94° ; d 0/4 1.1975, d 27/4 1.1819; n 27/D 1.5178.⁴²⁵
 OCHCH₂CH₂-, b_1 $66-70^\circ$; n 20/D 1.5079.⁹⁹
 OCHCH₂CHMe-, b_2 $59-60^\circ$; n 20/D 1.5025.⁹⁹
 OCHCH₂CHPh-, m . 44° ; b_1 $115-7^\circ$.⁹⁹
 H₂NCH₂CH₂-, HCl, m . 137° .⁷²⁹
 H₂NCH₂CH₂CH₂-, HCl, m . 130° .^{731.5}
 H₂N(CH₂)₄-, HCl, m . 150° .^{731.5}
 H₂N(CH₂)₆-, HCl, m . 115° .^{731.5}

$\text{H}_2\text{N}(\text{CH}_2)_{10}-, \text{HCl}, m. 145^\circ.^{731.5}$

$\text{NCCH}_2\text{CH}_2-, b_3 94^\circ; d_{20} 1.1212; n_{20/D} 1.4912.^{158a}$

3-Thienyl, $m. 43^\circ; b_1 84-6^\circ.^{95}$

2-Thenyl, $b_2 56-60^\circ.^{387}$

β -2-pyridylethyl, $b_{1.0} 95-7^\circ; n_{25/D} 1.5480.^{700}$

β -2-(5-ethylpyridyl)ethyl, $b_{9.5} 131-6^\circ; d_{25/4} 1.0664; n_{25/D} 1.5377.^{700}$

$\text{MeCH}=, b_{10} 103^\circ; d_{18} 1.1064; n_{16.5/D} 1.5212.^{46.3}$

Thiolpropionates, EtCOSR

Methyl, $b. 119-20^\circ.^{522}$

Ethyl, $m. -95^\circ; b. 136^\circ; d_{20/4} 0.9608; n_{20/D} 1.4584.^{743b}$

Butyl, $b_{15} 64.5^\circ.^{504}$

2-Thenyl, $b_2 79-83^\circ.^{387}$

$\text{EtCH}=, b_{12} 131^\circ.^{46.3}$

Thiolacrylates, $\text{CH}_2\text{:CHCOSR}$

Methyl, $b_{36} 44.0-45^\circ; n_{21.1/D} 1.5023.^{340}$

Ethyl, $b. 75-104^\circ;^{32.5} b_{14} 40.0-41.5^\circ; n_{21/D} 1.4896.^{340}$

Propyl, $b_4 37.0-39.7^\circ; n_{20.8/D} 1.4892.^{340}$

i-Propyl, $b_4 28.0-31.5^\circ; n_{21/D} 1.4821.^{340}$

Butyl, $b_1 42^\circ; n_{21/D} 1.4870.^{340}$

i-Butyl, $b_3 44.0-46^\circ; n_{21.2/D} 1.4837.^{340}$

t-Butyl, $b_8 44.5-45^\circ; n_{21.2/D} 1.4808.^{340}$

Dodec, $b_{0.4} 121-133^\circ;^{581} b_{11} 174-8^\circ.^{32.5}$

Ph, $b_{10} 150-180^\circ.^{32.5, 581}$

$\text{PhCH}_2, b_{0.8} 94-103^\circ;^{581} b_{0.08} 94-103^\circ.^{32.5}$

p- $\text{MeC}_6\text{H}_4-, b_{0.6} 89-94^\circ;^{581} b_{0.5} 68-95^\circ.^{32.5}$

$\text{HOOCCH}_2-, b_{0.06} 100-20^\circ.^{32.5}$

*Thiolbutyrates and Thiol-*i*-butyrates*

$\text{PrCOSBu}, b_{12} 80.1^\circ.^{504}$

t- $\text{C}_{14}\text{H}_{29}\text{SCOPr}, b_2 130-45^\circ.^{306}$

$(\text{PrCOS})_2\text{CHPr}, b_{15} 168^\circ.^{46.3}$

$\text{PrCOSPh}, b_9 122^\circ.^{495}$

i- $\text{PrCOSMe}, b. 140-44^\circ.^{522}$

i- $\text{PrCOSBu}, b_{12} 86.5^\circ.^{504}$

i- $\text{PrCOSPh}, b_{10} 129^\circ.^{495}$

Thiolmethacrylates and Thiocrotonates

MeCH:CHCOSPh, b_5 150°. ⁴⁹⁵

CH₂:CMeCOSPh, b_8 117°; n 20/D 1.5774. ⁴¹³

CH₂:CMeCOSCH₂Ph, b_6 130°; n 20/D 1.5681. ⁴¹³

Higher Esters

(Me₃CCOS)₂CHCMe₃, m . 51°; b_{12} 142°. ^{46.3}

AmCOSPh, b_{13} 152°. ⁴⁹⁵

Me₃CCH₂CH₂COSMe, b_{744} 188–94°, ⁶⁶² b_{745} 195°; n 25/D 1.4570. ⁶⁶³

HepCOSC₆H₁₁, b_2 103°. ^{590.5}

HepCOSPh, b_7 168°. ⁴⁹⁵

MeCH:CHCH:CHCOSPh, b_5 160°. ⁴⁹⁵

Thiollaurates, C₁₁H₂₃COSR

Methyl, b_1 112–5°; d 60/4 0.8734; n 25/D 1.4642, n 60/D 1.4496. ⁵⁶⁵

Ethyl b_1 115–7°; d 60/4 0.8645; n 25/D 1.4626, n 60/D 1.4478. ⁵⁶⁵

Propyl, b_1 126–8°; d 60/4 0.8610; n 25/D 1.4628, n 60/D 1.4478. ⁵⁶⁵

Butyl, b_1 133–5°; d 60/4 0.8595; n 25/D 1.4640, n 60/D 1.4493. ⁵⁶⁵

Thiolmyristates

Methyl, m . 34–5°; d 60/4 0.8668; n 60/D 1.4507. ⁵⁶⁵

Ethyl, b_1 134–6°; d 60/4 0.8609; n 25/D 1.4632, n 60/D 1.4488. ⁵⁶⁵

Propyl, b_1 148–50°; d 60/4 0.8568; n 25/D 1.4627, n 60/D 1.4485. ⁵⁶⁵

Butyl, b_1 149–51°; d 60/4 0.8570; n 25/D 1.4642, n 60/D 1.4501. ⁵⁶⁵

Thiopalmitates, C₁₅H₃₁COSR

Methyl, m . 45°; d 60/4 0.8644; n 60/D 1.4521. ⁵⁶⁵

Ethyl, b_1 172–5°; d 60/4 0.8547; n 25/D 1.4648, n 60/D 1.4513. ⁵⁶⁵

Propyl, m . 28°; d 60/4 0.8559; n 25/D 1.4642. ⁵⁶⁵

Butyl, m . 30°; d 60/4 0.8579; n 25/D 1.4646, n 60/D 1.4505. ⁵⁶⁵

Glyceryl, m . 71°. ⁵⁸⁷

Thiolstearates, C₁₇H₃₅COSR

Methyl, m . 51°; d 60/4 0.8624; n 60/D 1.4526. ⁵⁶⁵

Ethyl, m . 39°; d 60/4 0.8550; n 60/D 1.4514. ⁵⁶⁵

Propyl, m. 35°; d 60/4 0.8508; n 60/D 1.4509.⁵⁶⁵

Butyl, m. 32°; d 60/4 0.8534; n 60/D 1.4529.⁵⁶⁵

c-Hexyl, m. 44°.^{590.5}

Thiololeates, C₁₇H₃₃COSR

Propyl, b₁ 175–8°; d 60/4 0.8643; n 25/D 1.4713, n 60/D 1.4577.⁵⁶⁵

Thioloxalates

Methyl, m. 83.5°.³⁵⁶

Ethyl, m. 27.5°; b. 235°,³⁵⁶ 238–40°.⁶⁶⁷

Propyl, b₁₅ 158°.³⁵⁶

i-Amyl, b₁₉ 206°.³⁵⁶

Phenyl, m. 120°.³⁵⁶

Thiolmalonates

Ethyl, b₁₀ 135°.⁵⁵⁷

Phenyl, m. 94.5°.⁵⁵⁷

Thiolsuccinates

Ethyl, b₁₀ 165°,⁵⁵⁷ b. 270–1° dec.⁶⁴¹

Phenyl, m. 90.5°.⁵⁵⁷

Thiolglutarate

Cyclohexyl, m. 66°.¹⁶⁰

Thiolsebacate

Cyclohexyl, m. 69°.¹⁶⁰

Hexamethylene Esters of Monothioacids ^{414, 475b}

Succinic, HO₂C(CH₂)₂COS(CH₂)₆SCO(CH₂)₂CO₂H, m. 124°.

Glutaric, HO₂C(CH₂)₃COS(CH₂)₆SCO(CH₂)₃CO₂H, m. 107°.

Adipic, HO₂C(CH₂)₄COS(CH₂)₆SCO(CH₂)₄CO₂H, m. 124°.

Phthalic, HO₂C·C₆H₄COS(CH₂)₆SCOC₆H₄CO₂H, m. 138°.

α,β-Dibromothiopropionates, CH₂BrCHBrCOSR ³⁴⁰

Methyl, b_{0.3} 69.0–69.7°; n 21/D 1.5814.

Ethyl, b₁ 80.5–82.5°; n 21/D 1.5613.

Propyl, b_{7.5} 125–126°; n 20.1/D 1.5519.

i-Propyl, b_{0.7} 87.8–88.8°; n 20.1/D 1.5462.

Butyl, $b_{0.7}$ 103–105°; n 20.2/D 1.5436.
i-Butyl, $b_{0.7}$ 99.0–99.8°; n 20.6/D 1.5420.
t-Butyl, $b_{0.4}$ 61.8–66.5°; 21.1/D 1.5361.

TABLE 7.1
Chlorothioacetates

	$ClCH_2COSR$	$Cl_2CHCOSR$	Cl_3CCOSR
Methyl	b. 160°, b_{15} 58° ¹³	—	b_{20} 93.5° ⁶⁶⁹
Ethyl	b. 166–7° ⁴⁸⁵	b. 177–8° ⁴⁸⁵	—
Cyclohexyl	b_{14} 132° ¹⁶⁰	b_{12} 148° ¹⁶⁰	b_{12} 151° ¹⁶⁰
2-Me-cyclohexyl	b_{11} 137° ¹⁶⁰	—	$b_{0.05}$ 96° ¹⁶⁰
Phenyl	m. 45° ¹⁶⁴	—	—
<i>p</i> -Tolyl	m. 58°; b_{12} 153° ²⁴	—	—
<i>t</i> -Butyl	b_{21} 89°; d 25/4 1.1023 ¹⁶⁸	—	—
Cyclohexyl	—	—	$b_{0.5}$ 87° ^{590.5}

Esters of Perfluorothioacids

CF_3COSEt , b_{760} 90.5°; d 0/4 1.2766, d 25/4 1.2346; n 0/D 1.3888,
 n 25/D 1.3758.²⁹⁷
 CF_3CF_2COSEt , b_{760} 103°; d 0/4 1.3765, d 25/4 1.3284; n 0/D
 1.3707, n 25/D 1.3588.²⁹⁷
 $CF_3CF_2CF_2COSEt$, b_{760} 149°; d 0/4 1.4618, d 20/4 1.4203, n 0/D
 1.3631, n 20/D 1.3541.²⁹⁷
 $(CF_3COSCH_2CH_2)_2CH_2$, b_8 119°; d 0/4 1.3960, d 25/4 1.3624;
 n 0/D 1.4372, n 25/D 1.4268.²⁹⁷
 $(CF_3CF_2COSCH_2CH_2)_2CH_2$, b_8 128°; d 0/4 1.4758, d 25/4
 1.4388; n 0/D 1.4102, n 25/D 1.4001.²⁹⁷
 $(CF_3CF_2CF_2COSCH_2CH_2)_2CH_2$, b_8 142°; d 0/4 1.5613, d 25/4
 1.5212; n 0/D 1.3960, n 25/D 1.3864.²⁹⁷
 $(CF_2COSEt)_2$, b_8 108°.²⁹⁶
 $CF_2(CF_2COSEt)_2$, b_8 122°; d 0/4 1.4178, d 25/4 1.3852; n 0/D
 1.4446, n 25/D 1.4349.²⁹⁷
 $EtSCOCF_2CF_2CF_2COOH$, b_8 131°; n 25/D 1.4070; chloride b_{43}
 101°; n 25/D 1.4016.²⁹⁷

Miscellaneous Esters

$C_{17}H_{35}CH(Me)COSEt$, $b_{0.4}$ 180–90°.^{580.5}
 Et carbethoxyundecanethiolate, $b_{0.8}$ 165–70°.^{580.5}

- $3\text{-C}_4\text{H}_9\text{S}\cdot\text{COSMe}$, m. 43° .⁴⁰¹
 $\text{MeCHClCH}_2\text{COSPh}$, b_{10} 139° .⁴⁹⁵
 $\text{HOCH}_2\text{CH}:\text{C}(\text{CH}_2\text{OH})\text{COSEt}$, b_2 $142-7^\circ$.^{32.5}
 $\text{MeCOCH}_2\text{COSCM}_3$, b_3 55° ; $n_{25/D}$ 1.4808.¹⁵²
 $\text{MeCOCH}_2\text{CMe}_2\text{COSPh}$, m. 57° .⁶⁸⁰
 $\text{BzNHCH}_2\text{COSEt}$, m. 86° .^{353.5}
 $\text{BzNHCH}_2\text{COSCHMe}_2$, m. 81° .^{353.5}
 $\text{H}_2\text{NCH}_2\text{CH}_2\text{COSPh}$, HCl , m. 132° .⁷³¹
 $\text{H}_2\text{NCHMeCOSCH}_2\text{CH}_2\text{NHAc}$, HCl , m. 176° .⁷³⁰
 $\text{H}_2\text{NCMe}_2\text{COSMe}$, b_{32} $84-7^\circ$.⁴⁷⁶
 $\text{H}_2\text{NCMe}_2\text{COSEt}$, b_{29} $89-90^\circ$; HCl , m. 193° .⁴⁷⁶
 $\text{H}_2\text{NCMe}_2\text{COSCHMe}_2$, b_4 $60-1^\circ$; HCl , m. 160° .⁴⁷⁶
 $\text{Me}_2\text{CHCH}(\text{NH}_2)\text{COSCH}_2\text{CH}_2\text{NHAc}$, HCl , m. 211° with decomposition.⁷³⁰
 $\text{H}_2\text{NCPH}_2\text{COSCH}_2\text{CH}_2\text{CH}_2\text{NEt}_2$, m. 230° with decomposition.¹⁹²
 $4,3\text{-HO}(\text{MeO})\text{C}_6\text{H}_3\text{CH}(\text{NH}_2)\text{CSNH}_2$, m. 163° .^{1c}
 Benzyl 8-caffeine-8-carbothiolic acid, m. 176° .²⁶³
 $\text{PhCH}_2\text{COSPh}$, m. 40° ; b_3 161° .⁴⁹⁵
 $\text{PhCH}_2\text{COSCH}_2\text{CH}_2\text{NEt}_2$, b_{20} 180° ; HCl , m. 97° .⁶⁸⁵
 $\text{PhCHEtCOSCH}_2\text{CH}_2\text{NEt}_2$, b_8 $170-1^\circ$; ^{191, 685} HCl , m. 105° .⁶⁸⁵
 $\text{PhCHPrCOSCH}_2\text{CH}_2\text{NEt}_2$, b_8 $172-3^\circ$,¹⁹¹ $170-5^\circ$.⁶⁸⁵
 $\text{PhCH}(\text{CHMe}_2)\text{COSCH}_2\text{CH}_2\text{NEt}_2$, b_6 $160-1^\circ$,¹⁹¹ b_4 160° ; HCl , m. 125° .⁶⁸⁵
 $\text{PhCHBuCOSCH}_2\text{CH}_2\text{NEt}_2$, b_4 $169-70^\circ$.^{191, 685}
 $\text{PhCH}(\text{CH}_2\text{CH}_2\text{CHMe}_2)\text{COSCH}_2\text{CH}_2\text{NEt}_2$, b_6 $165-6^\circ$,¹⁹¹ 175° .⁶⁸⁵
 $\text{PhCH}(\text{C}_6\text{H}_{11})\text{COSCH}_2\text{CH}_2\text{SMe}$, m. 53° ; $b_{0.65}$ 175° ; MeI , m. 121° .⁵⁵⁵
 $\text{Ph}_2\text{CHCOSCH}_2\text{CH}_2\text{NEt}_2$, b_4 $199-200^\circ$; ^{191, 685} HCl , m. 115° .⁶⁸⁵
 $\text{Ph}_2\text{CHCOSCH}_2\text{Ph}$, m. 64° .⁶⁰¹
 $(p\text{-BrC}_6\text{H}_4)_2\text{CHCOSCH}_2\text{CH}_2\text{NEt}_2$, HCl , m. 113° .⁴¹⁹
 $\text{Ph}_2\text{C}(\text{OMe})\text{COSCH}_2\text{CH}_2\text{NMe}_2$, HCl , m. 225° .⁴¹⁹
 $\text{Ph}_2\text{C}(\text{OMe})\text{COSCH}_2\text{CH}_2\text{NEt}_2$, HCl , m. 181° .⁴¹⁹
 $\text{Ph}_2\text{C}(\text{OEt})\text{COSCH}_2\text{CH}_2\text{NMe}_2$, HCl , m. 220° .⁴¹⁹
 $\text{Ph}_2\text{C}(\text{OEt})\text{COSCH}_2\text{CH}_2\text{NEt}_2$, HCl , m. 201° .⁴¹⁹
 $\text{Ph}_2\text{C}(\text{OCHMe}_2)\text{COSCH}_2\text{CH}_2\text{NMe}_2$, HCl , m. 217° .⁴¹⁹
 $\text{Ph}_2\text{C}(\text{OCHMe}_2)\text{COSCH}_2\text{CH}_2\text{NEt}_2$, HCl , m. 183° .⁴¹⁹
 $\text{Ph}_2\text{C}(\text{OBu})\text{COSCH}_2\text{CH}_2\text{NMe}_2$, HCl , m. 227° .⁴¹⁹
 $\text{Ph}_2\text{C}(\text{OBu})\text{COSCH}_2\text{CH}_2\text{NEt}_2$, HCl , m. 187° .⁴¹⁹
 $\text{Ph}_2\text{C}(\text{OAm-}i)\text{COSCH}_2\text{CH}_2\text{NMe}_2$, HCl , m. 223° .⁴¹⁹

$\text{Ph}_2\text{C}(\text{OAm-}i\text{)}\text{COSCH}_2\text{CH}_2\text{NEt}_2$, HCl, m. 155° .⁴¹⁹
 $\text{Ph}_2\text{C}(\text{OCH}_2\text{CH:CH}_2)\text{COSCH}_2\text{CH}_2\text{NMe}_2$, HCl, m. 155° .⁴¹⁹
 $\text{Ph}_2\text{C}(\text{OCH}_2\text{CH:CH}_2)\text{COSCH}_2\text{CH}_2\text{NEt}_2$, HCl, m. 120° .⁴¹⁹
 PhCH:CHCOSEt , b_1 $120\text{--}40^\circ$.^{32.5, 581}
 PhCH:CHCOSPh , m. 78° .⁴⁹⁵
 $\text{PhCH:CHCOSC}_6\text{H}_4\text{Me-}p$, m. 79° .⁴⁹⁵
 $\text{PhCH:CHCOSCH}_2\text{Ph}$, m. 70° .⁶⁰¹
 $\text{Ph}_2\text{C:CHCOSCH}_2\text{CH}_2\text{NEt}_2$, HCl, m. 138° .⁴¹⁹
 $1\text{-PhC}_5\text{H}_8\text{COSEt}$, b_{3-4} 134° .⁴⁴¹
 $1\text{-PhC}_5\text{H}_8\text{COSCH}_2\text{CH}_2\text{NEt}_2$, $b_{0.05}$ $122\text{--}3^\circ$; HCl, m. 140° .²⁵⁵
 137.5 .⁴⁴¹
 $1\text{-PhC}_5\text{H}_8\text{COSCH}_2\text{CH}_2\text{CH}_2\text{NEt}_2$, HCl, m. 133° .⁴⁴¹
 $\text{PhCH:C}(\text{COSEt})_2$, b_1 $177\text{--}9^\circ$; n 25/D 1.6180.¹⁵²

Esters of Thiolbenzoic Acid, PhCOSR

Methyl, m. 56° ; ⁵⁵³ b. $231\text{--}2^\circ$,⁵²² b_{25} 134° ; d 25/4 1.1348.⁵⁵³
 Ethyl, b. $252\text{--}3^\circ$,^{575a, 724} 251° , $b_{2.5}$ $83\text{--}4^\circ$,⁷⁴⁴ b_{12} 117° ,⁷⁴ b_{11} 146° ,⁵⁵³
 b_{52} $155\text{--}6^\circ$,^{743b} b. $241\text{--}3^\circ$; ⁶⁴¹ d 20/4 1.1003,^{743b} d 25/4 1.0945 ⁵⁵³
 1.0978 ; n 25/D 1.5578,⁷⁴⁴ 1.5721.^{754b}
 Propyl, b_{13} 114° ; d 25/4 1.0693.⁵⁵³
 Butyl, b_{23} 160° ; d 25/4 1.0483.³⁷⁵
i-Butyl, b_{20} 150° ; d 25/4 1.0426.³⁷⁵
s-Butyl, b_{23} 151° ; d 25/4 1.04757.³⁷⁵
t-Butyl, b_{11} 127° ,⁵⁸⁶ b_{28} 110° ; d 25/4 1.0437.³⁷⁵
c-Hexyl, b_1 130° .^{590.5}
 Methylene, m. 119.5° .¹¹³
 Ethylene, m. 96° .²⁴⁷
 Trimethylene, m. 50.3° .⁵⁸⁴
 β -Hydroxyethyl, b_7 134° ; d 20/4 1.209; n 20/D 1.5942.⁵²¹
 β -Aminoethyl, HCl, m. 167° .⁷²⁹
 γ -Bromopropyl, b_1 $148\text{--}9^\circ$; d 25/4 1.4140; n 25/D 1.5950.³⁵⁹
 Phenyl, m. 56.6° ,⁵⁸³ 56° .^{74, 495, 622}
 Benzyl, m. 39.5° ,^{241, 532, 533} 38° ; b_7 185° .⁴⁹⁵
p-Tolyl, m. 75° ,⁶²² 72° ,⁶⁷⁷ 76° .⁴⁹⁵
p-Methoxyphenyl, m. 97° .⁶⁷⁷
p-Ethoxyphenyl, m. 106° .⁶⁷⁷
p-Bromophenyl, m. 85° .⁴⁹⁵
 2,4-Nitrochlorophenyl, m. 124° .⁴⁵¹
 3-Thienyl, $\text{C}_4\text{H}_3\text{S-}$, m. 70° .⁹⁵

2-Thenyl, $C_4H_3S \cdot CH_2-$, $b_{2.5}$ 155° .³⁸⁷

Benzal, $PhCH$, m. 138° .^{46.3, 113}

$-CH_2CONHC_{10}H_7-\beta$, m. 163° .⁴⁹⁵

Esters of Substituted Thiolbenzoic Acids

Of Miscellaneous Thiolbenzoic Acids

ClC_6H_4COSPh , *o*, m. 60° ; *p*, m. 183° .⁴⁹⁵

p- $ClC_6H_4COSC_6H_4Me$ -*p*, m. 110° .⁴⁹⁵

p- $ClC_6H_4COSC_6H_4Cl$ -*p*, m. 137° .^{582a}

p- FC_6H_4COSEt , b. $224-5^\circ$.²²⁶

p- FC_6H_4COSPr , b_6 $106-10^\circ$.²²⁶

p- FC_6H_4COSBu , b_8 $130-3^\circ$.²²⁶

p- $MeOC_6H_4COSPh$, m. 95° ,⁴⁹⁵ 93.2° .^{582a}

p- $MeOC_6H_4COSC_6H_4Me$ -*p*, m. 65.5° .^{582a}

p- $MeOC_6H_4COSC_6H_4OMe$ -*p*, m. 134° .^{582a}

p- $MeOC_6H_4COSC_6H_4NO_2$ -*p*, m. 156° .¹³⁵

3,4- $CH_2O_2=C_6H_3COSPh$, m. 185° .⁴⁹⁵

o- $HOC_6H_4COSC_6H_{11}$, m. 57° .^{590.5}

o- HOC_6H_4COSPh , m. 55° ; Ac., m. 86° .⁴⁹⁵

p- $AcOC_6H_4COSPh$, m. 85° .⁴⁹⁵

2,4- $HO(H_2N)C_6H_3COSEt$, m. 96° ; $AcNH-$, m. 157.5° .³²⁷

p- $EtSO_2C_6H_4COSMe$, m. 88° .⁵⁴¹

$O_2NC_6H_4COSPh$, *o*, m. 100° ; *m*, m. 132° .⁴⁹⁵

Of *p*-Nitrothiolbenzoic Acid

Methyl, m. 97° .^{285, 371}

Ethyl, m. 68° .^{285, 286, 371}

Propyl, m. 31° .²⁸⁵

Butyl, m. 15° .²⁸⁵

Ethylene, m. 204° .⁵⁸⁴

β -Chloroethyl, m. 92° .²⁸⁵

$O(CH_2CH_2)_2$, m. 106.5° .⁵⁸⁴

$S(CH_2CH_2)_2$, m. 119.4° .⁵⁸⁴

Phenyl, m. 160° ,⁴⁹⁵ 159.2° ,^{582a} 158° .²⁷⁰

Benzyl, m. 85.4° ,⁵⁸⁴ 82° .³⁷¹

Tolyl, *o*, m. 91° ; *m*, m. 96° ; *p*, m. 115° ,²⁷⁰ 114° .^{495, 582a}

Naphthyl, α , m. 123° ; β , m. 184° .²⁷⁰

p- $NO_2C_6H_4$, m. 153.5° .¹³⁵

p- $MeOC_6H_4$, m. 125° .¹³⁵

β -Dimethylaminoethyl, HCl , m. 194.2° .¹⁴⁰

β -Piperidinoethyl, m. 55° ; HCl, m. 176° .¹⁴⁰
 β -(2-Methylpiperidino) ethyl, HCl, m. 165.9° .¹⁴⁰
 β -Morpholinoethyl, HCl, m. 211° .¹⁴⁰
 γ -Dimethylaminopropyl, HCl, m. 127° .¹⁴⁰
 γ -Piperidinopropyl, HCl, m. 207.5° .¹⁴⁰
 γ -(2-Methylpiperidinopropyl, HCl, m. 186° .¹⁴⁰
 γ -Morpholinopropyl, m. 64° ; HCl, m. 202° .¹⁴⁰
 γ -Diethylaminobutyl, m. 162° .¹⁴⁰
 Ester of vitamin B₁, D, m. 135° .⁴⁷⁹

Of *p*-Aminothiobenzoic Acid

Methyl, m. 114° .²⁸⁵
 Ethyl, m. 79.5° .^{285, 286}
 Propyl, m. 61° .²⁸⁵
 Butyl, m. 38° .²⁸⁵
 β -Dimethylaminoethyl, phosphate, m. 189.2° .¹⁴⁰
 β -Piperidinoethyl, m. 123.5° ; phosphate, m. 206° .¹⁴⁰
 β -(2-Methylpiperidino)ethyl, m. 99.5° ; phosphate, m. 197.8° .¹⁴⁰
 β -Morpholinoethyl, m. 162° ; phosphate, m. 208° .¹⁴⁰
 γ -Diethylaminopropyl, phosphate, m. 210.6° .¹⁴⁰
 γ -Piperidinopropyl, m. 61° ; phosphate, m. 211.2° .¹⁴⁰
 γ -(2-Methylpiperidino) propyl, phosphate, m. 224° .¹⁴⁰
 γ -Morpholinopropyl, phosphate, m. 135.6° .¹⁴⁰
 $\text{Et}_2\text{NCH}_2\text{CH}_2\text{CHMe-}$, phosphate, m. 151° .¹⁴⁰
 δ -Diethylaminobutyl, phosphate, m. 200.8° .¹⁴⁰

Of *p*-Butylaminothiobenzoic Acid ¹⁴⁰

β -Dimethylaminoethyl, 2 HCl, m. 161.5° .
 β -Diethylaminoethyl, 2 HCl, m. 145.6° .
 β -Piperidinoethyl, m. 67° ; 2 HCl, m. 203.4° .
 β -(2-Methylpiperidino)ethyl, sesquiphosphate, m. $112-24^\circ$.
 β -Morpholinoethyl, m. 68° ; 2 HCl, m. 199.2° .
 γ -Diethylaminopropyl, 2 HCl, m. 139.8° .
 γ -Piperidinopropyl, 2 HCl, m. 188.4° .
 γ -(2-Methylpiperidino)propyl, 2 HCl, m. 173.4° .
 γ -Morpholinopropyl, m. 52° ; 2 HCl, m. 197.2° .

Of Other *p*-N-alkylaminothiobenzoates ¹⁴⁰

p -PrNHC₆H₄COSCH₂CH₂NEt₂, 2 HCl, m. 153.5° .
 p -AmNHC₆H₄COSCH₂CH₂NEt₂, picrate, m. 121.2° .
 p -HeptylNHC₆H₄COSCH₂CH₂NEt₂, citrate, m. 124° .

p -HO(CH₂)₅NHC₆H₄COSCH₂CH₂NEt₂, m. 73.6°.

2,4-Dinitrothiolbenzoic esters have been noted in chapter 2, Volume I, under identification of mercaptans.

Esters of Thioltoluic Acids

Ethyl, *o*, b₁₅ 133°; d 25/4 1.048, *p*, b₁₈ 150°; d 25/4 1.0670.⁶¹¹
p-Tolyl, *p*, m. 123.8°.^{582a}

Esters of Thiolnaphthoic Acids, C₁₀H₇COSR

α-C₁₀H₇COSPh, m. 121°.⁴⁹⁵
 α-C₁₀H₇COSC₁₀H₇-α, m. 126.2°.^{582a}
 β-C₁₀H₇COSC₆H₁₁, m. 64°.^{590.5}
 β-C₁₀H₇COSC₁₀H₇-β, m. 167.5°.^{582a}

1,2,3,4-Tetrahydrothiolnaphthoates ⁶⁴³

C₁₀H₁₁COSEt, α, b₇ 152–3°; β, b₈ 158°.
 C₁₀H₁₁COSCH₂CH₂NEt₄, HCl α, m. 142–4°; β, m. 119–21°.

Thiolphthalates

C₆H₄(COSR)₂, Me., m. 124°; ⁵⁷⁸ Ph, m. 101°.¹²⁶
 C₆H₄(COSEt)COOEt, b₁₀ 194°.⁵⁷⁸
 C₆H₄(COOEt)COSMe, b₁₀ 209°; d 1.1923.⁵⁷⁸
 C₆H₄(COOMe)COSEt, b₁₀ 209°; d 1.1906.⁵⁷⁸

$$\begin{array}{c} \diagup \text{C(SR)}_2 \diagdown \\ \text{C}_6\text{H}_4 \quad \quad \quad \text{O} \\ \diagdown \text{CO} \diagup \end{array}$$
 Ph, m. 85°.^{126, 695} β-C₁₀H₇, m. 154°.⁶⁹⁵

Thioimino Esters

HC(:NH)SCH₂Ph, HCl, m. 180°.³²⁴
 HC(:NPh)SEt, b. 230–40°.⁷¹⁰
 HC(:NC₆H₄Me-*p*)SEt, b. 252°.⁶⁵⁶
 MeC(:NH)SCH₂COOH, m. 99°; HCl, m. 112°; Et ester, HCl, 102°.³²⁴
 MeC(:NH)SPh, HCl, m. 120°.²¹
 MeC(:NH)SCH₂Ph, HCl, m. 155°.³²⁴
 MeC(:NH)SAc, HCl.³⁵⁰
 MeC(:NMe)SMe, b₇₄₈ 132–3°; d₂₀ 0.9459; n 20/D 1.492; HI, m. 119°.³⁹⁹
 MeC(:NPh)SMe, b. 244.6°,^{705d, 706} 246°.³⁵⁰

- $\text{MeC}(:\text{NPh})\text{SEt}$, b. $255-7^\circ$.⁷⁰⁶
 $\text{MeC}(:\text{NPh})\text{SPr}$, b. $270-3^\circ$.⁷⁰⁶
 $\text{MeC}(:\text{NPh})\text{SCHMe}_2$, b. 273° .⁷⁰⁶
 $\text{MeC}(:\text{NPh})\text{SCH}_2\text{CHMe}_2$.⁷⁰⁶
 $\text{MeC}(:\text{NPh})\text{SC}_3\text{H}_5$, b. $> 270^\circ$ with decomposition.⁷⁰⁶
 $\text{MeC}(:\text{NCH}_2\text{Ph})\text{SMe}$, b₄ $115-8^\circ$; d₂₃ 1.0575; n 23/D 1.5652;
 MeI, m. 120° .³⁹⁹
 $\text{MeC}(:\text{NC}_6\text{H}_4\text{Me})\text{SEt}$, o, b. $261-2^\circ$; p, b. $271-3^\circ$.⁷¹⁰
 $\text{PhC}(:\text{NH})\text{SEt}$, HCl, m. 188° ; ^{55a} HI, m. 142° .^{55a, 69}
 $\text{PhC}(:\text{NH})\text{SPh}$, HCl, m. 178° .²¹
 $\text{PhC}(:\text{NH})\text{SCH}_2\text{Ph}$, HCl, m. 181° .^{55a}
 $\text{PhC}(:\text{NMe})\text{SMe}$, b₈ 106° ,⁷⁵ b₄ 118° ; ^{399,480} HCl, m. 129° ; ⁷⁵ HI,
 m. 105° .³⁹⁹
 $\text{PhC}(:\text{NPh})\text{SMe}$, m. 64° ,^{480, 506} 66° .³⁹⁵
 $\text{PhC}(:\text{NPh})\text{SCH}_2\text{Ph}$, m. 53° .^{506, 592}
 $[\text{PhC}(:\text{NPh})\text{SCH}_2]_2$, m. 76° .⁵⁰⁶
 $\text{PhC}(:\text{NPh})\text{SBz}$, m. 108° .¹³⁶
 $2,4\text{-(HO)}_2\text{C}_6\text{H}_3\text{C}(:\text{NH})\text{SMe}$, m. 199° ; HCl, m. 245° .³⁶⁴
 $2,4\text{-(HO)}_2\text{C}_6\text{H}_3\text{C}(:\text{NH})\text{SEt}$, m. 199° ; HCl, m. 231° .³⁶⁴
 $2,4\text{-(HO)}_2\text{C}_6\text{H}_3\text{C}(:\text{NH})\text{SBu}$, m. 174° ; HCl, m. 228° .³⁶⁴
 $2,4\text{-(HO)}_2\text{C}_6\text{H}_3\text{C}(:\text{NH})\text{SPh}$, m. 158° ; HCl, m. 222° .³⁶⁴
 $2,4,6\text{-(HO)}_3\text{C}_6\text{H}_2\text{C}(:\text{NH})\text{SMe}$, m. 226° ; HCl, m. 256° ; H₂O, m.
 71° .³⁶⁴
 $p\text{-MeOC}_6\text{H}_4\text{C}(:\text{NMe})\text{SMe}$, m. 60° ; HI, m. 115° .⁷⁵
 $p\text{-MeOC}_6\text{H}_4\text{C}(:\text{NPh})\text{SMe}$, m. 170° .⁵⁹¹
 $o\text{-AcNHC}_6\text{H}_4\text{C}(:\text{NH})\text{SMe}$, m. 111° .³¹⁷
 $p\text{-AcNHC}_6\text{H}_4\text{C}(:\text{NH})\text{SEt}$, m. 98° .³¹⁷
 $p\text{-(NH}_2\text{SO}_2\text{)}_2\text{C}_6\text{H}_4\text{C}(:\text{NH})\text{SCH}_2\text{Ph}$, HCl, m. 193° .^{171, 580}
 $p\text{-(NH}_2\text{SO}_2\text{)}_2\text{C}_6\text{H}_4\text{C}(:\text{NPh})\text{SCH}_2\text{Ph}$, HCl, m. 105° .^{171, 580}
 $m\text{-MeC}_6\text{H}_4\text{C}[:\text{NC}(:\text{NH})\text{C}_6\text{H}_4\text{Me-}m]\text{SEt}$, m. 136° .^{336e}
 $p\text{-MeC}_6\text{H}_4\text{C}[:\text{NC}(:\text{NH})\text{C}_6\text{H}_4\text{Me-}p]\text{SEt}$, m. 154° .^{336e}
 $[\text{C}(:\text{NEt})\text{SEt}]_2$, b. $126-9^\circ$,^{705b} 250° with decomposition.⁷⁰⁹
 $[\text{C}(:\text{NMe})\text{SPr}]_2$, b. $170-5^\circ$.^{705b}
 $[\text{CH}_2\text{C}(:\text{NH})\text{SPh}]_2$, 2 HCl, m. 145° ; ²¹ 2HBr, m. 233° .²⁴⁷
 $\text{C}_6\text{H}_4[\text{C}(:\text{NH})\text{SEt}]_2\text{-1,3}$, 2 HCl, m. 190° .^{452, 547}

Oximinothioesters

- $\text{HC}(:\text{NOH})\text{SEt}$, m. 111° .³²⁴
 $\text{HC}(:\text{NOH})\text{SBu}$, m. 91° .³²⁴
 $\text{HC}(:\text{NOH})\text{SCH}_2\text{Ph}$, m. 117° .³²⁴

THIONESTERS, $\text{RCS}\cdot\text{OR}'$ *Thionacetates*

Methyl, b. $86-9^\circ$, ^{173b} $85-90^\circ$, ⁴⁷⁸ 88° , ^{173b}, ^{173c} $88-91^\circ$; ^{612a} d 0/4 1.0075, d 21/4 0.9842, ^{173b} d 28/4 0.9002, ^{612a} n 23/D 1.46062. ^{173b}
 Ethyl, b. $109-10^\circ$, ^{173b} $105-10^\circ$, ⁴⁷⁸ $105-7^\circ$; ^{612a} d 0/4 0.9816, ^{173b} d 17/4 0.8980, ^{612a} d 19/4 0.9618; n 19/D 1.46389; ^{173c} magnetic susceptibility 0.6098. ²¹⁶
 Propyl, b. $125-30^\circ$; d 28/4 0.8952. ^{612a}
i-Propyl, b. $119-22^\circ$; d 22/4 0.8901; n 22/D 1.4501. ^{612a}
 Butyl, b. $146-9^\circ$; d 29/4 0.8883; n 28/D 1.4196. ^{612a}
i-Butyl, b. $135-40^\circ$; d 26/ 4 0.8875; n 26/D 1.4316. ^{612a}
 Amyl, b₅₅ $72-4^\circ$; d 23/4 0.8639. ^{612a}
 Phenyl, b₃₈ $90-4^\circ$; d 20/4 0.9914. ^{612a}
 Benzyl, b₂₇ $115-20^\circ$; d 28/4 1.0296. ^{612a}

Thionpropionates

Methyl, b. $110-5^\circ$. ⁴⁷⁸
 Ethyl, b. $128-30^\circ$, ⁴⁷⁸ $125-9^\circ$, ^{612a} $130-2^\circ$, ^{173b} 131° ; ^{173c} d 0/4 0.9639, ^{173b} d 19/4 0.9431, ^{173c} d 20/4 0.8912; ^{612a} n 19/D 1.46281. ^{173c}
 Propyl, b. $139-44^\circ$; d 28/4 0.8835. ^{612a}
i-Propyl, b. $137-40^\circ$; d 28/4 0.8714. ^{612a}
 Butyl, b. $164-7^\circ$; d 28/4 0.8618. ^{612a}
i-Butyl, b. $153-7^\circ$; d 28/4 0.8678. ^{612a}
 Amyl, b₈₀ $84-6^\circ$; d 22/4 0.8595. ^{612a}
 Benzyl, b₂₈ $132-6^\circ$; d 28/4 1.0009. ^{612a}

Miscellaneous Thionesters

i-BuCSOMe, b. $145-8^\circ$; d 0/4 0.9577, ^{173b} d 12.5/4 0.9460; n 25/D 1.46727. ^{173c}
i-BuCSOEt, b. $160-5^\circ$; d 0/4 0.9549, ^{173b} d 12.5/4 0.9436; n 12.5/D 1.45569. ^{173c}
i-AmCSOMe, b. $160-70^\circ$. ^{173b}
 $\text{C}_6\text{H}_{11}\text{CSOMe}$, b₁₂ $90-100^\circ$. ^{173b}
 OctCSOMe, b₁₂ $115-20^\circ$. ^{173b}
 $\beta\text{-C}_{10}\text{H}_7\text{CSOEt}$, b₈₀ $188-94^\circ$. ^{612a}

Thionbenzoates, PhCSOR

Methyl, b₁₀ $110-12^\circ$, ^{173c} b₁₄ $144-4.5^\circ$, ⁶⁶⁸ b₂₆ $112-5^\circ$, ^{612a} b₃₂₀ $195-7^\circ$; ⁴⁷⁸ d 28/4 1.0710; n 29/D 1.5606. ^{612a}

Ethyl, b_{3-5} 124–7°; ^{612a} b_{300} 181°; ⁴⁷⁸ b . 240°; d 20/4 1.0452. ^{612a}
 Propyl, b_{29} 127–32°; d 28/4 1.0133; n 28/D 1.5289. ^{612a}
i-Propyl, b_{27} 117–22°; d 27/4 1.0060; n 28/D 1.5241. ^{612a}
 Butyl, b_{23} 137–42°; d 28/4 0.9732; n 28/D 1.5293. ^{612a}
i-Butyl, b_{27} 133–7°; d 28/4 0.9694; n 27/D 1.5049. ^{612a}
 γ -Bromopropyl, b_1 145–6°. ³⁵⁹
 2-Thenyl, b_{25} 155°. ³⁴⁹

Thionphenylacetates ^{612a}

Methyl, b_{83} 145–9°; d 28/4 1.0551; n 30/D 1.5612.
 Ethyl, b_{99} 170°; d 12/4 1.0142; n 25/D 1.9276.
 Propyl, b_{25} 130–3°; d 27/4 1.0139; n 29/D 1.5104.
i-Propyl, b_{50} 140–5°; d 22/4 1.0078; n 25/D 1.5026.
 Butyl, b_{36} 155–60°; d 25/4 0.9930; n 28/D 1.5138.
i-Butyl, b_{25} 138–43°; d 28/4 1.0010; n 28/D 1.5065.
i-Amyl, b_{50} 168–9°; d 23/4 0.9801; n 25/D 1.4902.
 Benzyl, b_{26} 180–5°; d 26/4 1.0866.

p-Thiontoluates, MeC_6H_4CSOR ^{612a}

Methyl, b_{150} 170–3°; d 26/4 1.0478.
 Ethyl, b_{70} 140–5°; d 20/4 0.9992.
 Propyl, b_{23} 130–5°; d 26/4 0.9858; n 23/D 1.5289.
i-Propyl, b_{48-50} 138–42°; d 22/4 0.9880.
 Butyl, b_{23} 150–2°; d 22/4 0.9905; n 23/D 1.5315.
i-Butyl, b_{38-40} 144–8°; d 25/4 0.9757; n 23/D 1.5215.
i-Amyl, b_{32} 155–8°; d 22/4 0.9856; n 23/D 1.5252.
 Benzyl, b_{21} 185–90°; d 22/4 1.0648.

Dithionoxalates, $(\cdot CSOR)_2$ ^{612a}

Methyl, b_{21} 50–2°.
 Ethyl, b_{32} 80–2°; d 21/4 1.0565.
i-Propyl, b_{43} 91–3°.

DITHIOACIDS AND ESTERS

Dithioacids

$MeCSSH$, b_{85} 66°; ^{590.5} b_{15} 37°; d_{20} 1.24; ³²² $K = 2.8 \times 10^{-3}$; ²⁸⁸
 magnetic susceptibility 0.5904. ²¹⁶
 $EtCSSH$, b_{17} 48°; d_{20} 1.12. ³²²
 $PrCSSH$, b_{13} 59°; d_{19} 1.08. ³²²
i- $BuCSSH$, b_{33} 84°; d_{19} 1.008. ³²²

i-AmCSSH, b_{10} 84° ; d_{22} 0.98.³²²
 PhCSSH, oil.³⁰⁹
p-MeC₆H₄CSSH, m. 27° .⁷⁹
o-HOC₆H₄CSSH, m. $48-50^\circ$.³⁰⁹
 2,4-(HO)₂C₆H₃CSSH, m. 131° .⁴⁴⁹
 2,3,4-(HO)₃C₆H₂CSSH, m. 154° .⁴⁴⁸
 Dithioisonicotinic Acid, K salt, m. 270° .⁴⁰⁴
 (MeCS)₂S, m. 225° .^{76b, 77}
 (PhCS)₂S₂, m. 92.5° .^{320a}

Dithioesters

(HCSSMe)₃, m. 105.5° .^{438a}
 (HCSSEt)₃, b_{11} 115° , b_{19} $131-2^\circ$.^{323a}
 (HCSSPr)₃, m. 39° .^{438a}
 (HCSSCH₂Ph)₃, m. 77° and 154.5° .^{438a}
 MeCSSMe, b_{760} 142° ,^{173b, 173c, 323a, 323b} b_{70} 71° , b_{95} $80-1^\circ$; ^{323a, 323b}
 d 21/4 1.096.^{173c, 323a, 323b}
 MeCSSEt, b_{11} $42-3^\circ$,^{323b} b_{23} 61° ,⁴⁷⁷ b . $128-32^\circ$; ^{612c} d 16/4
 1.036,^{323b} d 28/4 0.9807; n 28/D 1.5303,^{612c} n 20/D 1.5700.⁴⁷⁷
 MeCSSCH₂CHMe₂, b_{23} $86-87^\circ$; n 20/D 1.5440.⁴⁷⁷
 EtCSSMe, b_{11} 47° , b . $159-60^\circ$; d 21/4 1.047.^{323a, 323b}
 EtCSSEt, b_{10} $60-1^\circ$,^{285b} b_{20} $70-2^\circ$,⁴⁷⁷ b . $150-5^\circ$; d 27/4 0.9711;
 n 27/D 1.5259,^{612c} n 20/D 1.5542.⁴⁷⁷
 EtCSSCMe₃, b_{13} 70° .⁴⁷⁷
 C₆H₁₁CSSMe, b_3 90° .⁸¹
 C₆H₁₁CSSEt, b_5 106° .⁸¹
 C₆H₁₁CSSPr, b_3 106° .⁸¹
 C₆H₁₁CSSBu, b_5 145° .⁸¹
 PhCSSMe, b . $275-80^\circ$, b_{20} $154-7^\circ$,³⁰⁹ b_3 118° .⁵⁴¹
 PhCSSEt, b_{13} $158-62^\circ$, b_{19} $165-8^\circ$,³⁰⁹ b_{70} $122-5^\circ$.^{612c}
 PhCSSCH₂CH₂CH₂Br, m. $112-4^\circ$; b_1 $148-50^\circ$.³⁵⁹
 PhCSSCH₂Ph, b_3 $179-80^\circ$.⁷⁴⁶
 PhCSSCH₂COOH, m. 128° .^{315a}
 PhCH₂CSSMe, b_{760} 208° ; b_{12} 149° ,^{323a, 323b} b_1 120° ; ⁵⁴¹ d 24/4
 1.1389.^{323a, 323b}
 PhCH₂CSSEt, b_{45} $140-4^\circ$; d 20/4 1.0462.^{612c}
 PhCH₂CSSCH₂COOH, m. 79° .³⁹¹
p-MeC₆H₄CSSMe, b_3 130° .⁷⁹
p-MeC₆H₄CSSEt, b_3 132° ,⁷⁹ b_{85} $160-5^\circ$; d 17/4 1.0085,^{612c} d 20/4
 1.1173.⁷⁹

p -MeC₆H₄CSSBu, b_8 169°; d 20/4 1.0700.⁷⁹
 p -MeC₆H₄CSSCH₂C₆H₄NO₂- p , m . 70.5°.⁷⁹
 α -C₁₀H₇CSSMe, m . 54°; b . 210°.^{323b}
 α -C₁₀H₇CSSEt, m . 40°.^{323b}
 β -C₁₀H₇CSSEt, b_{45} 200–5°.^{612c}
 o -HOC₆H₄CSSMe, m . 10–20°.³⁰⁹
 p -HOC₆H₄CSSMe, m . 61°.³⁴⁹
 p -HOC₆H₄CSSEt, m . 57°; Bz., m . 80°; p -O₂NBz., m . 119°.³⁴⁹
 $(\cdot$ CSSMe)₂, m . 100.9°; $b_{0.1}$ 210°; d 20/4 1.619, isomer, m . 71.6°;
 d 20/4 1.658; ²¹⁷ *trans.*, m . 101.5°; *cis*, m . 71.5°.³⁰⁷
 $(\cdot$ CSSEt)₂, b_{42} 90–3°.^{612c}

p-BROMOPHENACYL ESTERS ^{80a}



MeCSSR, m . 97°. o -HOC₆H₄CSSR, m . 123°.
 p -H₂NC₆H₄CSSR, m . 175°. 3,4-MeO(HO)C₆H₃CSSR, m . 132°.

TRITHIO-ORTHOFORMIC ESTERS, HC(SR)₃

Methyl, m . 16°; b_9 96°.^{323c} b_{12} 103–4°.²⁹ b . 220°; ^{323c} n 15/D
 1.5696.²⁹
 Ethyl, b_{10} 116°.^{314b} b_{11} 124–5°.^{314b, 323c} b_{12} 119°.^{314b} 126.5–8°.²⁹
 b_{21} 133°.^{314b} b . 235° dec.; ^{323c} d 20/4 1.053.^{314b}
 Propyl, b_9 151°.⁶¹³ b_{12} 158–60°.²⁹
 Butyl, b_{12} 188–90°.²⁹
t-Butyl, m . 64.5°, b_4 115–7°.²⁹
 Allyl, b_{19} 120–2°.^{323c}
 Dodecyl, m . 37°.²²⁸
 Phenyl, m . 40°.^{314b} 39.5°.^{246a} 39°.³⁰⁸
 Benzyl, m . 103°.^{29, 369} 102.5°.^{323c} 98°.¹⁷⁷
 p -Tolyl, m . 111°.¹² 109°.^{246a}
 α -Naphthyl, m . 134°.^{323c}
 HC(SCH₂CO₂H)₃, m . 168–71°.^{320b} 173°.^{314a}
 Ethylene, m . 105°.³³¹

Other Trithio-ortho Esters ⁶⁸⁰

MeC(SPh)₃, m . 146°.
 MeC(SC₆H₄Me-*m*)₃, m . 118°
 MeC(SC₆H₄Me-*m*)₂SPh, m . 104°.
 MeC(SCH₂Ph)₃, m . 67°.
 PhC(SPh)₃, m . 87°.

TRISELENO-ORTHOFORMATES ⁴¹

HC(SeMe)₃, b₂₆ 90°.
 HC(SeEt)₃, b₂₆ 148–50°.
 HC(SePr)₃, b₂₆ 180–2°.

PERTHIOESTERS

RCOSSR'

MeCOS₂Me, b₁₂ 55–6°; d₂₀ 1.1831; n 20/D 1.5353; MR 32.1.^{74.5}
 MeCOS₂Et, b₁₁ 70–1°.⁷²
 MeCOS₂Ph, b₁₁ 146–48°.⁷²
 MeCOS₂CH₂Ph, m. 59°.^{74.5}
 MeCOS₂C₁₀H₇-β, m. 59°.⁷²
 MeCOS₂CH₂CH₂Cl, b₁₉ 118–20°.⁷²
 PhCOS₂Ph, m. 53°.⁷²
 PhCOS₂C₁₀H₇-β, m. 69°.⁷²
 MeCOS₃Me, b₁₁ 90–1°; d₂₀ 1.2868; n 20/D 1.5973; MR 40.8.^{74.5}
 MeCOS₃Et, b₁₁ 102–4°.⁷²
 MeCOS₃Ph, oil.⁷²
 MeCOS₃CH₂Ph, n 20/D 1.6366.^{74.5}
 MeCOS₃C₁₀H₇-β, m. 64°.⁷²
 PhCOS₃C₁₀H₇-β, m. 54°.⁷²
 MeCOS₄Et, d₂₀ 1.3105; n 20/D 1.6229; MR 53.9.^{74.5}
 PhCOS₅C₆H₃(NO₂)_{2-2,4}, m. 114°.⁷²

THIOAMIDES

Aliphatic Thioamides

Thioformamides

HCSNH₂, m. 29°.^{543, 737}
 HCSNHMe, b. 125°.⁷²¹
 HCSNHEt, b₁₀ 125°,^{310a, 310c} b₁₄ 125°,^{512, 721} b₄₀ 140–50°.⁵¹²
 HCSNHCH₂CH₂CHMe₂, b₈ 140°,⁷²¹ b₁₀ 143–6°.⁶⁹³
 HCSNH(CH₂)₃CHMe₂, b₂ 125°.⁷²¹
 HCSNHCH₂CH₂OH, b_{1.5} 135°.⁷²¹
 HCSNHCH₂CH₂NMe₃OH, m. 238°.^{333e}
 HCSNHC₆H₁₁, m. 82°.⁶
 HCSNHPh, m. 138°,^{333c, 576, 720, 721} 137°,^{505b} 137.5°,^{311d, 311e}
 134°.^{54c, 55c}

- $\text{HCSNHCH}_2\text{Ph}$, m. 65° ,⁷²¹ 68.2° .⁸³
 $\text{HCSNHCH}_2\text{COPh}$, m. 108° .⁵²⁶
 $\text{HCSNHC}_6\text{H}_4\text{Me}$, *o*, m. 101° ,⁵¹² 96° ; ⁶⁴² *p*, m. 173.5° .⁶⁴²
 $\text{HCSNHC}_6\text{H}_3(\text{CH}_3)_2$, m. 105° .²⁷²
 $\text{HCSNHC}_6\text{H}_4\text{OMe-}p$, m. 128° .^{310a}
 $\text{HCSNHC}_6\text{H}_4\text{NH}_2\text{-}o$, m. 77° .^{310c}
 2,3-Dimethyl-4(1-pyrazoliny) thioformanilide, m. 175° .^{310c}
 $(\text{HCSNHCH}_2)_2$, m. 147° .^{310a, 693, 721}
 $(\text{HCSNH})_2\text{C}_6\text{H}_4$, *o*, m. 77° ; ^{310a} *m*, m. 147° .⁷²¹
 HCSNMe_2 , b_{12} 97° ,^{721, 737} *b*. 228° ; *d* 0/4 1.047; MeI, m. 123° .⁷³⁷
 HCSNt_2 , b_{14} 117° ,⁷³⁷ b_{15} $112-3^\circ$.^{333c}
 HCSNPh_2 , m. 109° .⁷³⁷
 $\text{HCSN}(\text{CH}_2)_5$, b_{12} 149° ; MeI, m. 120° .⁷³⁷
 $\text{HCSN}(\text{CH}_2\text{CH}_2)_2\text{O}$, m. 68.5° .⁴⁶⁷
 2-Thioformamido-4,5-dimethyl-N-(triacetyl-L-arabinosido) aniline, m. 136° .³¹³
 2-Thioformamido-4,5-dimethyl-N-(triacetylribosido) aniline, m. 98° .³¹³
 N-4(2-Methyl-5-methylaminopyridyl) thioformamide, m. 193° .
^{332a, 333a, 333f}
 N-6-Quinolylthioformamide, m. 238° .^{333c, 721}
 N-5-(2-Methyl-4,6-dihydroxypyrimidylmethyl) thioformamide, m. 200° .³¹²
 N-5-(2-Methyl-4-aminopyrimidylmethyl) thioformamide, m. 190° .^{312, 721}

Thioacetamides

- MeCSNH_2 , m. 108.5° ,^{54c, 55b, 69, 115} 108° ,^{103, 311e, 543} 115° ,^{377a} 116° ; ³⁸⁰ HgCl_2 , m. 183° with decomposition.^{336c}
 MeCSNHMe , m. 58° .³⁹⁹
 MeCSNHBu , b_8 131.5° ,⁶²⁴ b_1 113° ; *n* 20/D 1.5392.⁴⁷⁷
 $\text{MeCSNHC}_6\text{H}_{11}$, m. 78° .^{437a}
 $\text{MeCSNHC}_3\text{H}_5$, b_{17} $135-6^\circ$.⁶⁰⁹
 MeCSNHPh , m. 76° ,^{341b, 374, 433} 75° .^{373, 505b, 582b, 609}
 $\text{MeCSNHCH}_2\text{Ph}$, m. 73.2° ,⁸³ 71° ,³⁹⁹ 65.3° ,⁶¹³ 63° ; ^{749a} b_2 $158-62^\circ$.⁶¹³
 $\text{MeCSNHC}_6\text{H}_4\text{Me}$, *o*, m. 68° ; ^{705d, 710} *m*, m. 64° ,³¹⁷ 43° ; ^{749a} *p*, m. 128° ,⁵⁷ 132° ,^{705d, 710} 131° .³⁴²
 $\text{MeCSNHC}_6\text{H}_4\text{Et}$, *o*, m. 70° ; *p*, m. 59° .^{483.5}
 $\text{MeCSNHC}_6\text{H}_3\text{Me}_2$, m. 80° ,²⁷² 95° .³⁴²

- $\text{MeCSNHC}_{10}\text{H}_7\text{-}\alpha$, m. 111° ,^{341b} 96° .⁵⁷
 $\text{MeCSNHC}_{10}\text{H}_7\text{-}\beta$, m. 146° ,^{341b} HgCl_2 , m. 118° .^{336c}
 $\text{MeCSNHC}_6\text{H}_4\text{Cl}$, *o*, m. 63° ; ^{483.5} *p*, m. 143° ,⁶⁰⁹ 142° .^{749a}
 $\text{MeCSNHC}_6\text{H}_4\text{Br}$, *m*, m. 76° ; *p*, m. 153° .^{749a}
 $\text{MeCSNHC}_6\text{H}_4\text{I}$ -*p*, m. 149° .^{749a}
 $\text{MeCSNHC}_6\text{H}_4\text{OMe}$, *o*, m. 53° ; *m*, m. 114° .^{749a}
 $\text{MeCSNHC}_6\text{H}_4\text{OEt}$ -*p*, m. 100° ,⁶⁰⁹ 114° .^{749a}
 $\text{MeCSNHC}_6\text{H}_4\text{NO}_2$, *o*, m. 109° ; *m*, m. 98° ; *p*, m. 175° .³¹⁷
 $\text{MeCSNHC}_6\text{H}_4\text{CO}_2\text{Me}$ -*o*, m. 111° .³¹⁷
 $\text{MeCSNHC}_6\text{H}_4\text{CO}_2\text{Et}$ -*p*, m. 98° .³¹⁷
 $\text{MeCSNHC}_6\text{H}_4\text{N}:\text{NC}_6\text{H}_5$ -*p*, m. 144° .³¹⁷
 MeCSNMe_2 , b. 238° .^{173b, 173c}
 MeCSNEt_2 , m. 81° ; ⁶³ b_{4-5} $102-5^\circ$.^{437b}
 $\text{MeCSN}(\text{CH}_2\text{CH}_2)_2\text{O}$, m. $88.9-90.3^\circ$,^{437a} 80° ; ⁵⁴¹ b_{24} $125-32^\circ$; *n* $25/\text{D}$ 1.4853 .⁸⁵
 $\text{MeCSN}(\text{CH}_2)_5$, m. 61° ,^{602.5, 606} 57° ,^{437a,} 58° .⁴⁸⁹
 MeCSNMePh , m. 59° ; b. 290° with decomposition.^{705d}
 MeCSNEtPh , m. 49° .³¹⁷
 $\text{MeCSNEtCH}_2\text{Ph}$, $b_{1.5}$ $161-2^\circ$; *d* $19/4$ 1.068 ; *n* $19/\text{D}$ 1.6015 .⁸³
 $\text{MeCSN}(\text{Ph})\text{CH}_2\text{Ph}$, m. 83° .³¹⁷
 $(\text{MeCSNH})_2\text{CH}_2$, m. 146° .⁵⁵⁶
 $(\text{MeCSNHCH}_2^\bullet)_2$, m. 160° .⁴⁸⁹
 $(\text{MeCSNHCH}_2\text{CH}_2^\bullet)_2$, m. 119° .⁴⁸⁹
 $(\text{MeCSNHCH}_2\text{CH}_2\text{CH}_2^\bullet)_2$, m. 99° .⁴⁸⁹

Some Other Aliphatic Thioamides

- EtCSNH_2 , m. 43° ,^{326 377a, 543} 42° ; b_2 97° .⁴⁷⁷
 $\text{EtCSNHCH}_2\text{CH}:\text{CH}_2$, b_{12} 136° .⁶⁰⁹
 $\text{EtCSNHCH}_2\text{CHBrCH}_2\text{Br}$, m. 179° .⁶⁰⁹
 EtCSNHPh , m. 67.5° .⁶⁰⁹
 $\text{EtCSNHCH}_2\text{Ph}$, m. 45.5° ; b_{30} $213-5^\circ$.⁸³
 $\text{EtCSNHC}_6\text{H}_4\text{CH}_3$ -*p*, m. 53° .³¹⁷
 $(\text{EtCSNHC}_6\text{H}_4^\bullet)_2$, m. 229° .⁶⁰⁹
 $\text{EtCSNHC}_6\text{H}_3(\text{OH})_{2-2,4}$, m. 96° .³⁶¹
 $\text{EtCSNHC}_6\text{H}_2(\text{OH})_{3-2,4,6}$, m. 152° .³⁶¹
 $\text{EtCSNHC}_6\text{H}_4\text{OEt}$ -*p*, m. 75° .⁶⁰⁹
 EtCSNMe_2 , *d* $19/4$ 0.9969 ; *n* $19/\text{D}$ 1.55328 .^{173c}
 $\text{CH}_2:\text{CHCSNHC}_6\text{H}_2(\text{OH})_{3-2,3,4}$, m. 206° .³⁶¹
 $\text{MeCCl}_2\text{CSNH}_2$, m. 54° .⁶⁹⁴
 PrCSNHBu , b_6 $142-4^\circ$.^{437b}

PrCSNHPh , m. 33° .⁶⁰⁹
 $\text{PrCSNHCH}_2\text{Ph}$, m. 44° ; b_{14} $199\text{--}200^\circ$.⁸³
i- $\text{PrCSNHCH}_2\text{Ph}$, m. 48.3° ; b_{30} $203\text{--}5^\circ$.⁸³
 BuCSNHPh , m. 39° .^{749c}
 $\text{BuCSNHC}_6\text{H}_4\text{Me-}p$, m. 70° .^{749c}
 $\text{BuCSNHC}_6\text{H}_4\text{OMe-}p$, m. 63° .^{749c}
 $\text{BuCSNHC}_6\text{H}_4\text{Cl-}p$, m. 102° .^{749c}
 $\text{BuCSNHC}_6\text{H}_4\text{Br-}p$, m. 112° .^{749c}
 BuCSNPh_2 , m. 148° .^{749c}
 $\text{BuCSNHC}_{10}\text{H}_7\text{-}\beta$, m. 80° .^{749c}

p- $\text{BuCSNHC}_6\text{H}_4\text{NHCSBu}$, m. 199° .^{749c}
 $\text{AmCSNHCH}_2\text{Ph}$, m. 43.5° ; b_{17} $204\text{--}5^\circ$.⁸³
i- AmCSNHPh , m. 63° .⁶⁰⁹
 $\text{C}_9\text{H}_{19}\text{CSNH}_2$, m. 97° .^{300, 563, 566}
 $\text{C}_{11}\text{H}_{23}\text{CSNH}_2$, m. 83° .^{463, 566}
 $\text{C}_{13}\text{H}_{27}\text{CSNH}_2$, m. 88° .^{463, 566}
 $\text{C}_{15}\text{H}_{31}\text{CSNH}_2$, m. 94° .^{463, 566}
 $\text{C}_{16}\text{H}_{33}\text{CSNH}_2$, m. 99° .⁵⁶³
 $\text{C}_{17}\text{H}_{35}\text{CSNH}_2$, m. 97° ,^{463, 566} 98° .⁵⁶³

Thiobenzamides

PhCSNH_2 , m. 117.4° ,^{582b} 117° ,^{54c} 116° ; $55c$, 155 , $377a$, $378c$, 380 HgCl_2 ,
 m. 197° .^{336c}
 PhCSNHMe , m. 81.5° ,⁷⁵ 80° ,^{315b} 79° .⁶⁰⁹
 PhCSNHEt , m. 29° ; $815b$ b_8 $177\text{--}8^\circ$.⁷⁵
 $\text{PhCSNHC}_{12}\text{H}_{25}$, m. 45° .^{281a}
 $\text{PhCSNHCH}_2\text{CH:CH}_2$, b_{17} 215° .⁶⁰⁹
 $\text{PhCSNHCH}_2\text{CHBrCH}_2\text{Br}$, m. 209° .⁶⁰⁹
 $\text{PhCSNHC}_6\text{H}_{11}$, m. 92° ,^{6, 653} 89.5° .⁵¹¹
 PhCSNHPh , m. 104° ,^{315b} 102° ,⁶⁰⁹ 101.6° ,^{582b} 99° ,^{75, 705c} 98.5° ,⁶⁰⁹
 98° ,^{54c} 97° ,^{55c} 96.5° ,^{55d, 395, 396} 96° .^{505a}
 PhCSN(Ph)Bz , m. 108° .⁵⁰⁶
 $\text{PhCSNHC}_6\text{H}_4\text{Me}$, *o*, m. 86° ; ⁶⁷⁴ *p*, m. 129.5° ,⁴³³ 129° .^{57, 505a}
 $\text{PhCSNHC}_6\text{H}_3\text{Me}_2$, m. 90° .²⁷²
 $\text{PhCSNHC}_{10}\text{H}_7$, α -m. 150° ,⁵⁹³ 148.5° ,^{341b} 147.5° ; ⁵⁷ β -m. 162° ; ⁵⁹³
 HgCl_2 , m. 187° .^{336c}
 $\text{PhCSNHCH}_2\text{Ph}$, m. 88.6° ,⁸³ 88° ,^{315c} 85° .⁴⁶⁶
 $\text{PhCSNHCH}_2\text{COOH}$, m. 150° ; ²⁵¹ Me ester, m. 74° ; ³⁹¹ Et ester,
 m. 40° ; ²⁵¹ amide, 2 forms, m. 119° and 137° .³⁹¹
 $\text{PhCSNHCH}_2\text{CONHEt}$, m. 117° .³⁹¹

- $\text{PhCSNHCH}_2\text{CONHCH}_2\text{Ph}$, m. 124° .³⁹¹
 $\text{PhCSNHCH}_2\text{CON}(\text{CH}_2\text{CH}_2)_2\text{O}$, m. 121° .³⁹¹
 PhCSNHCHMeCOOH , Me ester, m. 101° ; amide, m. 204.5° .³⁹¹
 $\text{PhCSNHCH}(\text{CH}_2\text{CH}_2\text{SMe})\text{COOEt}$, m. 83° .³⁹¹
 PhCSNHCHPhCONH_2 , m. 161° .³⁹¹
 $\text{PhCSNHCH}(\text{CH}_2\text{Ph})\text{COOH}$, Et ester, m. 76° ; amide, m. 157° .³⁹¹
 $\text{PhCSNHCH}(\text{CH}_2\text{C}_6\text{H}_4\text{OH-}p)\text{CONH}_2$, m. 185° .³⁹¹
 $\text{PhCSNHCH}(\text{CONH}_2)\text{CH}_2\text{CONH}_2$, m. 175° .³⁹¹
 $\text{PhCSNHC}_6\text{H}_4\text{NO}_2\text{-}m$, m. 150° .⁵⁹⁴
 $\text{PhCSNHC}_6\text{H}_4\text{NH}_2\text{-}p$, m. 147° .⁵⁹⁴
 $\text{PhCSNHC}_6\text{H}_3(\text{Me})\text{NH}_2\text{-}4,2$, m. 197° .⁵⁷
 $\text{PhCSNHC}_6\text{H}_3(\text{OH})_2\text{-}2,4$, m. 176° .³⁶¹
 $\text{PhCSNHC}_6\text{H}_4\text{OMe-}p$, m. 109° .^{377d, 378c}
 $\text{PhCSNHC}_6\text{H}_4\text{OEt-}p$, m. 127° .⁶⁰⁹
 $\text{PhCSNH}(\text{C}_{10}\text{H}_6\text{OH-}4)\text{-}\alpha$, m. 206° .³⁶¹
 PhCSNHCN , m. 82° .⁵⁷⁶
 PhCSNCONHPh , m. 145° .⁵⁷⁶
 PhCSNMe_2 , m. 70° ,^{315c} 67° ; b_{18} 182° .^{377a}
 $\text{PhCSN}(\text{Et})_2$, m. 43.5° .^{315c}
 PhCSNPh_2 , m. 155° ,⁶⁰⁶ 151° ,^{54c} 149° .^{55c}
 $\text{PhCSN}(\text{CH}_2\text{CH}_2\text{Ph})_2$, m. 90° ; MeI, m. 92° .¹²³
 PhCSNMePh , m. 91° ,⁴⁸⁰ 101.5° .⁵⁴¹
 $\text{PhCSN}(\text{Et})\text{Ph}$, m. 98° .⁶⁰⁶
 $\text{PhCSN}(\text{Et})\text{CH}_2\text{Ph}$, $b_{3.5}$ $209\text{--}10^\circ$; d $19/4$ 1.108 ; n $19/4$ 1.6310 .⁸³
 $\text{PhCSN}(\text{Ph})\text{CH}_2\text{Ph}$, m. 120° ,³¹⁷ 122° .⁵⁹²
 $\text{PhCSN}(\text{CH}_2)_5$, m. 66° ,⁶⁰⁶ 65° .^{315b}
 $\text{PhCSN}(\text{CH}_2\text{CH}_2)_2\text{O}$, m. 137.5° ,¹²³ 136° .^{467, 541}
 $\text{PhCSN}(\alpha\text{-C}_{10}\text{H}_7)\text{CPh:NC}_{10}\text{H}_7\text{-}\alpha$, m. 157° .⁵⁹³
 $\text{PhCSN}(\beta\text{-C}_{10}\text{H}_7)\text{CPh:NC}_{10}\text{H}_7\text{-}\beta$, m. 117° .⁵⁹³
 $\text{PhCSN}(\text{CH}_2\text{CH}_2)_2\text{NCSPH}$, m. 266.5° .¹²³

Substituted Thiobenzamides

- $\text{ClC}_6\text{H}_4\text{CSNH}_2$, o , m. 63° ; ²¹² p , m. 124° .^{377b}
 $o\text{-ClC}_6\text{H}_4\text{CSNHCH}_2\text{Ph}$, m. 67° .⁸³
 $\text{BrC}_6\text{H}_4\text{CSNH}_2$, m , m. 120° ; p , m. 141.5° .^{377b}
 $p\text{-IC}_6\text{H}_4\text{CSNH}_2$, m. 153° .^{377b}
 $m\text{-O}_2\text{NC}_6\text{H}_4\text{CSNH}_2$, m. 131° ; ^{336b} HgCl_2 , m. 206° with decomposition.^{336c}
 $p\text{-O}_2\text{NC}_6\text{H}_4\text{CSNH}_2$, m. 157° ; ^{336b} HgCl_2 , m. 194° .^{336c}
 $\text{O}_2\text{NC}_6\text{H}_4\text{CSNHPh}$, m , m. 134.5° ; ^{336c, 594} p , m. 155° .⁵⁹⁴

p -O₂NC₆H₄CSNHCH₂Ph, m. 100.5°. ⁸³
 H_2 NC₆H₄CSNHPh, *m*, m. 131°; ⁵⁹⁴ *p*, m. 155°; ⁵⁹¹ 154°. ⁵⁹⁴
 p -H₂NC₆H₄CSN(CH₂CH₂)₂O, Ac., m. 211–5°. ⁵⁴¹
 p -EtSC₆H₄CSNHPh, m. 141°. ²⁵
 p -MeSO₂C₆H₄CSNH₂, m. 218°. ⁵⁴⁰
 p -EtSO₂C₆H₄CSN(CH₂CH₂)₂O, m. 186°. ⁵⁴¹

Other Aromatic Thioamides

m -MeC₆H₄CSNH₂, HgCl₂, m. 186°. ^{336c}
 m -MeC₆H₄CSNHC₆H₄Me-*m*, m. 110°. ^{336c}, ^{336e}
 p -MeC₆H₄CSNH₂, m. 168°; ^{377a}, ^{377b}, ⁶¹⁹ 155°; ⁷⁹ HgCl₂, m. 194°. ^{336c}
 p -MeC₆H₄CSNHMe, m. 55°. ^{377a}
 p -MeC₆H₄CSNHC₆H₁₁, m. 105°. ⁶⁵³
 p -MeC₆H₄CSNHPh, m. 141°. ²³⁴
 p -MeC₆H₄CSNHCH₂Ph, m. 88.5°. ⁸³
 p -MeC₆H₄CSNHC₆H₄Me-*p*, m. 166°; ²³⁴ 170.5°. ⁷⁹
 p -MeC₆H₄CSNHCOPh, m. 136°. ^{723b}
 p -MeC₆H₄CSN(CH₂CH₂)₂O, m. 109°, MeI, m. 154.5°. ¹²³
 α -C₁₀H₇CSNH₂, HgCl₂, m. 184°. ^{336c}
 α -C₁₀H₇CSNHC₆H₁₁, m. 98°. ⁶⁵³
 β -C₁₀H₇CSNH₂, m. 151°; ^{377a} HgCl₂, m. 221°. ^{336c}
PhCH₂CSNH₂, m. 99°; ⁹⁷ 98°; ^{54c}, ^{377a}, ³⁹¹ 97°; ^{54b}, ^{336c} MeI, m. 130.5°; ^{54b} HgCl₂, m. 160°. ^{336c}
PhCH₂CSNHMe, m. 63°. ^{377a}, ^{378c}
PhCH₂CSNHC₆H₁₁, m. 80°. ^{384b}
PhCH₂CSNHPh, m. 87.5°; ^{384b} 88°; ⁵⁷⁹ 87°; ⁶⁰⁹ 89°. ³⁴²
PhCH₂CSNHCH₂Ph, m. 85.5°. ^{384b}
PhCH₂CSNMe₂, m. 81°; ^{377a}, ^{378c} b₁₂ 184°. ^{377a}
PhCH₂CSNMePr, b_{1.5} 155–8°; n 24.5/D 1.5876. ¹⁴⁹
PhCH₂CSN(CH₂)₅, m. 78.5°; ^{384b} 80°. ⁶³⁶
PhCH₂CSN(CH₂CH₂)₂O, m. 80°; ^{384b}, ³⁹¹ 78.5°. ¹¹⁷
PhCH₂CSNHCH₂CO₂H, m. 142°. ³⁹¹
PhCH₂CSNHCH₂CONHCH₂Ph, m. 133°. ³⁹¹
PhCH₂CSNHCH₂CON(CH₂)₅, m. 120°. ³⁹¹
PhCH₂CSNHCHMeCOOH, Me ester, m. 73°; amide, m. 145°. ³⁹¹
PhCH₂CSNHCH₂CH(OEt)₂, b_{0.07} 155–8°. ⁹⁸
 p -ClC₆H₄CH₂CSNH₂, m. 129°. ^{377c}
 p -MeC₆H₄CH₂CSNMe₂, m. 72°. ³⁸¹
 p -EtC₆H₄CH₂CSNMe₂, b₂₀ 225°. ³⁸¹

- $\text{PhCH}_2\text{CH}_2\text{CSNH}_2$, m. 87° .^{377a}
 $\text{PhCH}_2\text{CH}_2\text{CSNMe}_2$, m. 56° .^{377a, 377d}
 $p\text{-FC}_6\text{H}_4\text{CH}_2\text{CH}_2\text{CSNMe}_2$, m. 58° , b_{26} 220° .³⁸¹
 $p\text{-ClC}_6\text{H}_4\text{CH}_2\text{CH}_2\text{CSNMe}_2$, m. 64° .³⁸¹
 $p\text{-BrC}_6\text{H}_4\text{CH}_2\text{CH}_2\text{CSNMe}_2$, m. 72° .³⁸¹
 $p\text{-IC}_6\text{H}_4\text{CH}_2\text{CH}_2\text{CSNMe}_2$, m. 113° .³⁸¹
 $p\text{-MeSC}_6\text{H}_4\text{CH}_2\text{CH}_2\text{CSNMe}_2$, m. 67° .³⁸¹
 $p\text{-MeC}_6\text{H}_4\text{CH}_2\text{CH}_2\text{CSNMe}_2$, m. 49° ; b_{18} 225° .³⁸¹
 $p\text{-EtC}_6\text{H}_4\text{CH}_2\text{CH}_2\text{CSNMe}_2$, m. 73° ; b_{12} $295\text{--}310^\circ$.³⁸¹
 $\text{PhCH}_2\text{CH}(\text{Me})\text{CSNH}_2$, m. 62° .^{377c}
 $\text{PhCH}_2\text{CH}_2\text{CH}_2\text{CSNH}_2$, m. 62° .^{377c}
 $\text{PhCH}_2\text{CH}_2\text{CH}_2\text{CSNMe}_2$, b. 205° .^{378c}
 $\alpha\text{-C}_{10}\text{H}_7\text{CH}_2\text{CSN}(\text{CH}_2\text{CH}_2)_2\text{O}$, m. 109° .^{514, 636}
 $\beta\text{-C}_{10}\text{H}_7\text{CH}_2\text{CSN}(\text{CH}_2)_5$, m. 87° .⁶³⁶
 $\beta\text{-[5,6,7,8-H}_4\text{C}_{10}\text{H}_7\text{CH}_2\text{CH}_2]\text{CSN}(\text{CH}_2\text{CH}_2)_2\text{O}$, m. 109° .¹⁴

Thiofuramides

- $\text{C}_4\text{H}_3\text{O}\cdot\text{CSNH}_2$, m. 127° .⁵¹¹
 $\text{C}_4\text{H}_3\text{O}\cdot\text{CSNHC}_6\text{H}_{11}$, m. 80° .⁵¹¹
 $\text{C}_4\text{H}_3\text{O}\cdot\text{CSN}(\text{CH}_2)_4$, m. 68° .⁵¹¹
 $\text{C}_4\text{H}_3\text{O}\cdot\text{CSN}(\text{CH}_2\text{CH}_2)_2\text{O}$, m. 65° .⁵¹¹

PYRIDINE DERIVATIVES

Thionicotinamides

- $\text{C}_5\text{H}_4\text{NCSNH}_2$, m. 181° .³⁶⁰

Thioisonicotinamides

- $\text{C}_5\text{H}_4\text{NCSNH}_2$, m. 210° .⁴⁰⁴
 $\text{C}_5\text{H}_4\text{NCSNHBu}$, m. 80° .⁴⁰⁴
 $\text{C}_5\text{H}_4\text{NCSNHC}_6\text{H}_{11}$, m. 174° .⁴⁰⁴
 $\text{C}_5\text{H}_4\text{NCSNHCH}_2\text{Ph}$, m. 134° .⁴⁰⁴
 $\text{C}_5\text{H}_4\text{NCSNHPh}$, m. 179° ,⁴⁰⁴ 182° .¹⁹⁸
 $\text{C}_5\text{H}_4\text{NCSN}(\text{CH}_2)_5$, m. 117° .⁴⁰⁴

Thiopicolinamides

- $\text{C}_5\text{H}_4\text{CSNH}_2$, m. 137° .³⁶⁰
 $\text{C}_5\text{H}_4\text{NCSNHPh}$, m. 52° .¹⁹⁷
 $\text{C}_5\text{H}_4\text{NCSNHC}_6\text{H}_4\text{Me}$, *o*, m. 68° ; *p*, m. 101° .¹⁹⁷
 $\text{C}_5\text{H}_4\text{NCSNHC}_{10}\text{H}_7\text{-}\alpha$, m. 132° .¹⁹⁷

$C_5H_4NCSNHC_6H_4N(Me)_2$ -*p*, m. 125°. ¹⁹⁷
 $C_5H_4NCSNHC_6H_4OH$ -*p*, m. 145°. ¹⁹⁷
p- $C_5H_4NCSNHC_6H_4NHCSC_5H_4N$, m. 215°. ¹⁹⁷
 $C_5H_4NCSNMePh$, m. 86°. ¹⁹⁷

HYDROXYTHIOAMIDES

$HOCH_2CSNH_2$, Bz., m. 103°. ⁵²⁷
 $HOCHMeCSNH_2$, Bz., m. 104°. ⁵²⁷
 $HOCMe_2CSNH_2$, Ac., m. 123°. ³
 $HOCHEtCSNH_2$, Bz., m. 106°. ⁵²⁷
 $PhCH(OH)CSNH_2$, Ac., m. 105°, ^{3, 377a} 104°; Bz., m. 139°. ³
o- $O_2NC_6H_4CH(OH)CSNH_2$, Ac., m. 145°; Bz., m. 173°. ³
 $AcOCH_2-(CHOAc)_4-CSNH_2$, m. 154°; $[\alpha]$ 20/D 63°. ⁵⁹
o- $HOC_6H_4CSN(CH_2CH_2)_2O$, m. 100°; MeI, m. 189°, EtI, m. 182°. ¹²³
p- $HOC_6H_4CSNHPh$, m. 165°, ⁴⁸¹ 164°. ⁵⁹¹
2,4-(HO) $_2C_6H_3CSNH$ Et, m. 96°. ³⁶¹
2,4-(HO) $_2C_6H_3CSNHPh$, m. 182°, ⁴⁸¹ 176°. ³⁶¹
2,4-(HO) $_2C_6H_3CSNHC_{10}H_7$ - β , m. 179°. ³⁶¹
2,4-(HO) $_2C_6H_3CSNH(C_{10}H_6OH-\alpha)-\beta$, m. 179°. ³⁶¹
2,3,4-(HO) $_3C_6H_2CSNH$ Et, m. 206° with decomposition. ³⁶¹
2,4,6-(HO) $_3C_6H_2CSNH$ Et, m. 152°. ³⁶¹
2,4,6-(HO) $_3C_6H_2CSNHPh$, m. 161°. ³³⁵
2,4-Me(HO) $C_6H_3CSNHPh$, m. 176°. ⁵⁹¹
3,4-Me(HO) $C_6H_3CSNHPh$, m. 165°. ⁵⁹¹
5,2-Me(HO) $C_6H_3CSNHPh$, m. 139°. ⁵⁹¹
 $HOC_6H_4CH_2CSN(CH_2CH_2)_2O$, *o*, m. 161°; ³⁸⁵ *m*, m. 84°. ⁶³⁶
1-(HO)- β - $C_{10}H_6CSNHPh$, m. 184°, ⁴⁸¹ 183°. ⁵⁹¹
4-(HO)- α - $C_{10}H_6CSNHPh$, m. 208°, ⁴⁸¹ 206°, ³⁶¹ 205°. ⁵⁹¹
2-(HO)- α - $C_{10}H_6CSNHPh$, m. 100°. ⁵⁹¹

ALKOXYTHIOAMIDES

$MeOCH_2CSNH_2$, m. 64°. ²⁰⁷
 $EtOCH_2CSNH_2$, m. 81°. ⁶⁵⁹
 $PrOCH_2CSNH_2$, m. 63°. ⁶⁵⁹
i- $BuOCH_2CSNH_2$, m. 61°. ⁶⁵⁹
p- $MeOC_6H_4CSNH_2$, m. 149°. ^{377b, 574}
p- $MeOC_6H_4CSNHMe$, m. 112°, ⁷⁵ 109°. ^{377a, 378c}
p- $MeOC_6H_4CSNMe_2$, m. 68.5°. ^{377a}
p- $MeOC_6H_4CSNHPh$, m. 154°. ⁶⁹⁶

- p -MeOC₆H₄CSNHCH₂Ph, m. 39°. ⁸³
 p -MeOC₆H₄CSNHC₆H₄Me, *o*, m. 95°; *p*, m. 157°. ⁶⁹⁶
 p -EtOC₆H₄CSNH₂, m. 161.5°. ²³⁵ 158°. ^{723b}
 p -EtOC₆H₄CSNHPh, m. 143°. ⁶⁹⁶
 p -EtOC₆H₄CSNHC₆H₄Me, *o*, m. 106°; *p*, m. 151°. ⁶⁹⁶
 p -EtOC₆H₄CSNHC₆H₃Me₂-2,4, m. 140°. ⁶⁹⁶
 p -EtOC₆H₄CSNHC₁₀H₇- α , m. 200°. ⁶⁹⁶
 p -O[C₆H₄CSN(CH₂CH₂)₂O]₂, m. 154°. ⁴⁷³
 p -MeOC₆H₄CH₂CSNMe₂, m. 76°. ^{377a, 378c}
 p -MeOC₆H₄CH₂CSNMe₂, b₁₂ 220°. ^{377a}
 m -MeOC₆H₄CH₂CSN(CH₂)₅, m. 84°. ⁶³⁶
2,4-(MeO)₂C₆H₃CH₂CSNHMe, m. 88°. ^{579, 609}
3,4-(MeO)₂C₆H₃CH₂CSNHMe, m. 130°. ³⁸²
3,4-(MeO)₂C₆H₃CH₂CSNMe₂, m. 121°. ^{377d, 382}
 p -PhOC₆H₄CH₂CSN(CH₂CH₂)₂O, m. 87°. ⁴⁷³
 o -PhCH₂OC₆H₄CH₂CSN(CH₂)₅, m. 87°. ⁶³⁶
 o -PhCH₂OC₆H₄CH₂CSN(CH₂CH₂)₂O, m. 119°. ⁶³⁶
3,4-(CH₂O)₂C₆H₃CH₂CSNHMe, m. 136°. ^{377d}
 p -MeOC₆H₄CH₂CH₂CSNMe₂, m. 70°. ^{381, 382}
3,4-Me(MeO)C₆H₃CH₂CH₂CSNMe₂, m. 83°. ³⁸¹
3,4-(MeO)₂C₆H₃CH₂CH₂CSNMe₂, m. 94°. ³⁸¹
 β -(α -EtOC₁₀H₈)CSNHPh, m. 200°. ⁶⁹⁶
 α -(4-MeOC₁₀H₈)CH₂CH₂CSNMe₂, b₁₈ 245°. ³⁸¹
3,4-CH₂(O₂)C₆H₃CH(OH)CSNH₂, Ac., m. 145°. ³
MeCOCH₂CSNHC₆H₄Me, *o*, m. 75°; *m*, m. 84°. ^{749a}

MISCELLANEOUS THIOAMIDES

- PhCH:CHSNH₂, m. 143.5°, ²⁰⁶ 112°. ⁴¹⁸
PhCBr:CBrcSNHC₆H₄Cl-*p*, m. 230°. ⁷⁵⁰
PhC:CCSNHMe, m. 80°. ^{749b}
PhC:CCSNHCH₂CH:CH₂, m. 61°. ^{749b}
PhC:CCSNHC₆H₄Me-*p*, m. 113°. ^{749b}
PhC:CCSNHC₆H₄Ph-*p*, m. 129°. ⁷⁵¹
PhC:CCSNHC₆H₄Cl-*m*, m. 116°; dimer, m. 228° with decomposition. ⁷⁵⁰
PhC:CCSNHC₆H₄Cl-*p*, m. 139°; dimer, m. 246° with decomposition. ⁷⁵⁰
PhC:CCSNHC₆H₄Br-*m*, m. 121°. ⁷⁵¹
PhC:CCSNHC₆H₄I-*p*, m. 141°. ⁷⁵¹
PhC:CCSNHC₆H₄OEt-*p*, m. 112°. ⁷⁵¹

$\text{PhC}:\text{CCSNHC}_{10}\text{H}_7\text{-}\alpha$, m. 185° .⁷⁵¹
 $p\text{-IC}_6\text{H}_4\text{C}:\text{CCSNHPh}$, m. 141° .⁷⁵¹
 $p\text{-PhC}_6\text{H}_4\text{C}:\text{CCSNHPh}$, m. 129° .⁷⁵¹
 $p,p'(\text{ClC}_6\text{H}_4\text{C}:\text{CCSNHC}_6\text{H}_4\cdot)_2$, m. 240° .⁷⁵⁰
 $p,p'(\text{IC}_6\text{H}_4\text{C}:\text{CCSNHC}_6\text{H}_4\cdot)_2$, m. 173° .⁷⁵¹
 $p,p'(\text{EtOC}_6\text{H}_4\text{C}:\text{CCSNHC}_6\text{H}_4\cdot)_2$, m. 200° .⁷⁵¹
 N-Phenyl-4(α -Naphthylphenyl)propiolamide, m. 185° .⁷⁵¹
 2-Benzothiazolylethylthioanilide, m. 127° .⁵⁷⁹

$\text{NC}\cdot\text{CSNH}_2$, m. 90° .¹⁰
 $\text{NC}\cdot\text{CSNHPh}$, m. 82° .⁵⁷⁶
 $\text{NC}\cdot\text{CH}_2\text{CSNH}_2$, m. 123° .³²⁵
 $\text{H}_2\text{NCHPhCSNHAc}$, m. 140° .^{1d}
 BzNHCHPhCSNH_2 , m. 192° .^{1e}
 $\text{PhCH}(\text{NHCHO})\text{CSNH}_2$, m. 181° .^{1d}
 $\text{NCCHPhNH}(\text{CH}_2)_4\text{NHCHPhCSNH}_2$, m. 128° .⁷⁶⁵
 $p\text{-MeOC}_6\text{H}_4\text{CH}(\text{NHCHO})\text{CSNH}_2$, m. 184° .^{1d}
 $4,3\text{-HO}(\text{MeO})\text{C}_6\text{H}_3\text{CH}(\text{NH}_2)\text{CSNHAc}$, m. 181° with decomposition.^{1d}
 $4,3\text{-HO}(\text{MeO})\text{C}_6\text{H}_3\text{CH}(\text{NHBz})\text{CSNHBz}$, m. 219° .^{1e}
 $\text{MeC}(\text{Ph})(\text{NH}_2)\text{CSNHAc}$, m. 148° .^{1d}
 $\text{Me}_2\text{NCH}_2\text{CH}_2\text{CHPhCSNH}_2$, m. 145° .⁵¹⁷
 $\text{Et}_2\text{NCH}_2\text{CH}_2\text{CHPhCSNH}_2$, HCl, m. 187° .⁹⁷
 $\text{Me}_2\text{NCH}_2\text{CH}_2\text{CH}(\text{C}_6\text{H}_4\text{Cl})\text{CSNH}_2$, o, m. 136° ; p, m. 144° .⁵¹⁷

THIOAMIDES OF POLYBASIC ACIDS

Oxalic

$\text{HOOC}\cdot\text{CSNHPh}$, m. 102° .⁵⁷⁶
 $\text{EtOOC}\cdot\text{CSNH}_2$, m. 64° .⁷¹³
 $\text{BuOOC}\cdot\text{CSNH}_2$, m. 58° .⁷¹³
 $\text{PhNHCO}\cdot\text{CSNH}_2$, m. 176° .⁵⁷⁶
 $\text{Me}_2\text{NCO}\cdot\text{CSNH}_2$, m. 121° .¹⁷
 $\text{Et}_2\text{NCO}\cdot\text{CSNH}_2$, m. 127° .¹⁷
 $\text{Pr}_2\text{NCO}\cdot\text{CSNH}_2$, m. 130° .¹⁷
 $(\text{CH}_2)_5\text{NCO}\cdot\text{CSNH}_2$, m. 67° .¹⁷
 $\text{Ph}_2\text{NCO}\cdot\text{CSNH}_2$, m. 220° .⁴⁸⁴
 $\text{H}_2\text{NCO}\cdot\text{CSNHPh}$, m. 170° .⁵⁷⁶
 $\overline{\text{CH}_2\text{CH}_2}\text{CHNHCO}\cdot\text{CSNHPh}$, m. 110° .²⁹³

$\text{PhNHCO} \cdot \text{CSNHPh}$, m. 145° .⁵⁷⁶
 $\text{EtOOC} \cdot \text{CSNHC}_6\text{H}_4\text{Cl-}o$, m. 40° ; b₅ $145\text{--}55^\circ$.^{483.5}
 $\text{MeNHCS} \cdot \text{CSNHMe}$, m. 140° .^{705b}
 $\text{EtNHCS} \cdot \text{CSNHet}$, m. 58° ,^{705b} 54° .⁷⁰⁹
 $\text{Me}_2\text{CHNHCS} \cdot \text{CSNHCHMe}_2$, m. 101° .⁵¹¹
 $\text{Me}_2\text{CHCH}_2\text{CH}_2\text{NHCS} \cdot \text{CSNHCH}_2\text{CH}_2\text{CHMe}_2$, m. 60° .^{705b}
 $\text{C}_{12}\text{H}_{25}\text{NHCS} \cdot \text{CSNHC}_{12}\text{H}_{25}$, m. 53° .^{437a}
 $\text{C}_6\text{H}_{11}\text{NHCS} \cdot \text{CSNHC}_6\text{H}_{11}$, m. 158° ,^{437a} 147° .⁵¹¹
 $\text{PhNHCS} \cdot \text{CSNH}_2$, m. 98° .^{576, 577}
 $\text{PhNHCS} \cdot \text{CSNHPh}$, m. 134° ,⁵⁷⁶ 133° .^{312, 705d}
 $\text{MeC}_6\text{H}_4\text{NHCS} \cdot \text{CSNHC}_6\text{H}_4\text{Me}$, *o,o'*-m. 123° ; *p,p'*-m. 250° .⁵⁷⁹
 $\text{ClC}_6\text{H}_4\text{NHCS} \cdot \text{CSNHC}_6\text{H}_4\text{Cl}$, *o,o'*, m. 175° .^{483.5}
 $\text{O}(\text{CH}_2\text{CH}_2)\text{NCS} \cdot \text{CSN}(\text{CH}_2\text{CH}_2)_2\text{O}$, m. 265° ,^{437a} 254° .⁴⁶⁷

Malonic

$\text{HOOCCH}_2\text{CSNHC}_3\text{H}_5$, m. 121° .^{749a}
 $\text{HOOCCH}_2\text{CSNHC}_6\text{H}_4\text{Me-}p$, m. 97° .^{749a}
 $\text{HOOCCH}_2\text{CSNHC}_{10}\text{H}_7$, α -m. 57° ; β -m. 69° .^{749a}
 $\text{HOOCCH}_2\text{CSNHCH}_2\text{Ph}$, m. 96° .^{749a}
 $\text{HOOCCH}_2\text{CSNHC}_6\text{H}_4\text{Cl-}p$, m. 114° .^{749a}
 $\text{HOOCCH}_2\text{CSNHC}_6\text{H}_4\text{Br}$, *m*, m. 101° with decomposition; *p*, m. 131° .^{749a}
 $\text{HOOCCH}_2\text{CSNHC}_6\text{H}_4\text{I-}p$, m. 133° .^{749a}
 $\text{HOOCCH}_2\text{CSNHC}_6\text{H}_4\text{OMe-}p$, m. 91° with decomposition.^{749a}
 $\text{HOOCCH}_2\text{CSNHC}_6\text{H}_4\text{OEt-}p$, m. 105° with decomposition.^{749a}
 $\text{CH}_2(\text{CSNH}_2)_2$, m. 212° with decomposition,⁴²⁸ 167° .⁷²⁶
 $\text{CH}_2(\text{CSNHPh})_2$, m. 149° .⁵⁷⁹
 $\text{CH}_2(\text{CSNHC}_6\text{H}_4\text{Me})_2$, *o*, m. 123° ; *p*, m. 145° .⁵⁷⁹
 $\text{BuCH}(\text{CSNHPh})_2$, m. 68° .⁵⁰¹
 $\text{PhCH}(\text{CO}_2\text{Et})\text{CSNH}_2$, m. 121° .⁹⁷
 $\text{PhCH}(\text{CSNHPh})_2$, m. 67° .⁵⁰¹
 $\text{AmCONHCH}(\text{CO}_2\text{H})\text{CSNH}_2$, m. 83° .¹⁴⁷
 $\text{PhCH}_2\text{CONHCH}(\text{CO}_2\text{H})\text{CSNH}_2$, m. 115° .¹⁴⁷

α,ω -Dibasic

$\text{HOOCCH}_2\text{CH}_2\text{CSNHPh}$, m. 107° .⁵⁷⁹

$\begin{array}{c} \text{CH}_2\text{CO} \\ | \quad \diagdown \\ \text{CH}_2\text{CS} \quad \text{NPh} \end{array}$, m. 117° .⁵⁷⁹
 $(\cdot\text{CH}_2\text{CSNH}_2)_2$, m. 189° .⁷²⁶

$(\cdot\text{CH}_2\text{CSNHCHMe}_2)_2$, m. 128° .⁵¹¹
 $(\cdot\text{CH}_2\text{CH}_2\text{CSNH}_2)_2$, m. 180° ,²⁰³ 172° with decomposition.²⁸⁴
 $(\cdot\text{CH}_2\text{CH}_2\text{CSNHOct})_2$, m. 114° .²⁸⁴
 $(\cdot\text{CH}_2\text{CH}_2\text{CSNHC}_6\text{H}_{11})_2$, m. about 168° .²⁸⁴
 $[\cdot\text{CH}_2\text{CH}_2\text{CSN}(\text{CH}_2)_5]_2$, m. 150° .²⁸⁴
 $\text{CH}_2(\text{CH}_2\text{CH}_2\text{CH}_2\text{CSNH}_2)_2$, m. 142° .⁴²⁹
 $(\cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CSNH}_2)_2$, m. 153° .⁴²⁹
 $\text{C}_6\text{H}_4(\text{CSNH}_2)_2$, *m*, m. 200° ; ⁴⁵² *p*, m. 263° .^{204, 452}
p- $\text{H}_2\text{NCSC}_6\text{H}_4\text{C}_6\text{H}_4\text{CSNH}_2$ -*p*, m. 250° .³⁶⁰

Tricarboxylic ^{749a}

$(\text{MeOOC})_2\text{CHCSNHC}_3\text{H}_5$, m. 43° .
 $(\text{MeOOC})_2\text{CHCSNHBu}$, m. 63° .
 $(\text{MeOOC})_2\text{CHCSNHAm}$, m. 53° .
 $(\text{EtOOC})_2\text{CHCSNHMe}$, m. 50° .
 $(\text{EtOOC})_2\text{CHCSNHEt}$, m. 52° .
 $(\text{EtOOC})_2\text{CHCSNHPr}$, m. 11° .

Acetyl Malonic ^{749a}

$\text{MeCOCH}(\text{COOEt})\text{CSNHPh}$, m. 83° .
 $\text{MeCOCH}(\text{COOEt})\text{CSNHC}_6\text{H}_4\text{Me}$, *m*, m. 80° ; *p*, m. 81° .
 $\text{MeCOCH}(\text{COOEt})\text{CSNHC}_{10}\text{H}_7$ -*α*, m. 84° .
 $\text{MeCOCH}(\text{COOEt})\text{CSNHC}_6\text{H}_4\text{OMe}$ -*p*, m. 98° .
 $\text{MeCOCH}(\text{COOEt})\text{CSNHC}_6\text{H}_4\text{OEt}$ -*p*, m. 88° .
 $\text{MeCOCH}(\text{COOEt})\text{CSNHC}_6\text{H}_4\text{Cl}$ -*p*, m. 79° .
 $\text{MeCOCH}(\text{COOEt})\text{CSNHC}_6\text{H}_4\text{Br}$, *m*, m. 82° ; *p*, m. 63° .
 $\text{MeCOCH}(\text{COOEt})\text{CSNHC}_6\text{H}_4\text{I}$ -*p*, m. 65° .

SELENAMIDES ^{377a}

MeCSeNH_2 , m. 126.5° .
 $\text{PhCH}_2\text{CSeNH}_2$, m. 92.5° .

THIOHYDRAZIDES

$\text{BuCSNH}\cdot\text{NMePh}$, m. 123° .⁷⁵⁶
 $c\text{-HexCSNH}\cdot\text{NMePh}$, m. 107° .⁷⁵⁶
 $\text{PhCSNH}\cdot\text{NHCpyridyl-3-}$, m. 142° .³⁴⁵
 $\text{PhCSNH}\cdot\text{NHCpyridyl-4-}$, m. 130° .³⁴⁵
 $o\text{-MeC}_6\text{H}_4\text{CSNH}\cdot\text{NHPh}$, m. 118° .^{754a}
 $\alpha\text{-C}_{10}\text{H}_7\text{CSNH}\cdot\text{NHPh}$, m. 152° .^{754a}
 $\text{PhCH}_2\text{CSNH}\cdot\text{NH}_2$, m. 71° .³⁴⁵

- $\text{PhCH}_2\text{CSNH}\cdot\text{NMePh}$, m. 81° .⁷⁵⁶
 $\text{PhCH}_2\text{CSNH}\cdot\text{N}:\text{CHC}_6\text{H}_3\text{Cl}_2\text{-2,4}$, m. 152° .³⁴⁵
 $\text{PhCH}_2\text{CSNH}\cdot\text{N}:\text{CHC}_6\text{H}_4\text{NO}_2\text{-}p$, m. 171° .³⁴⁵
 $\text{PhCH}_2\text{CSNH}\cdot\text{N}:\text{CHC}_6\text{H}_4\text{NHCOMe}$, m. 193° .³⁴⁵
 $\text{PhCH}_2\text{CSNH}\cdot\text{N}:\text{CHC}_6\text{H}_4\text{CO}_2\text{H-}o$, m. 167° .³⁴⁵
 $\text{PhCH}_2\text{CSNH}\cdot\text{N}:\text{CHC}_{10}\text{H}_7\text{-}\alpha$, m. 160° .³⁴⁵
 $\text{PhCH}_2\text{CSNH}\cdot\text{N}:\text{furyl-2}$, m. 98° .³⁴⁵
 $\text{HOC}_6\text{H}_4\text{CSNH}\cdot\text{NH}_2$, *o*, m. 102° ; *p*, m. 208° .³⁴⁵
 $p\text{-MeOC}_6\text{H}_4\text{CSNH}\cdot\text{NH}_2$, m. 126° .³⁴⁵
 $p\text{-MeOC}_6\text{H}_4\text{CSNH}\cdot\text{N}:\text{CHC}_6\text{H}_4\text{NHAc}$, m. 172° .³⁴⁵
 $3,4\text{-MeO(HO)C}_6\text{H}_4\text{CSNH}\cdot\text{NH}_2$, m. 148° .³⁴⁵
 $2\text{-FurylCSNH}\cdot\text{NH}_2$, m. 135° .³⁴⁵
 $2\text{-FurylCSNH}\cdot\text{N}:\text{CHfuryl-2}$, m. 138° .³⁴⁵
 $2\text{-FurylCSNH}\cdot\text{N}:\text{CHC}_6\text{H}_4\text{NHAc-}p$, m. 197° .³⁴⁵
 $2\text{-ThienylCSNH}\cdot\text{NH}_2$, m. 156° .³⁴⁵
 $2\text{-PyrrolylCSNH}\cdot\text{NH}_2$, m. 122° .³⁴⁵
 $2\text{-IndolylCSNH}\cdot\text{NH}_2$, m. 173° .³⁴⁵
 $p\text{-AcNHC}_6\text{H}_4\text{CSNH}\cdot\text{NH}_2$, m. 234° .³⁴⁵
 $p\text{-Me}_2\text{NC}_6\text{H}_4\text{CSNH}\cdot\text{NH}_2$, m. 170° .³⁴⁵
 Thioisonicotinic acid hydrazide, m. 134° .⁴⁰⁴
 Thiogalactonic acid phenylhydrazide, m. 175° ; $[\alpha]_{20/D} 31.5^\circ$.⁷⁶⁸
 D-Thiogluconic acid phenyl hydrazide, m. 179° ; $[\alpha]_{20/D} 59.4^\circ$.⁷⁶⁸

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CHAPTER 2.

Thiocarbonic Acids and Derivatives

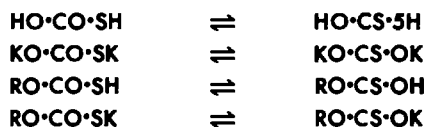
Introduction

By substituting one or more sulfur atoms for the oxygens of carbonic acid, five thio-acids are possible:

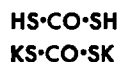
HO·CO·OH	HO·CO·SH	HO·CS·OH	HO·CS·SH	HS·CO·SH	HS·CS·SH
	<i>Thiol-</i>	<i>Thion-</i>	<i>Thiol-thion</i>	<i>Dithiol-</i>	<i>Trithio-</i>

As in the thio-acetic acids, the prefix thiol-, is used for those in which the hydroxyl oxygen is replaced by sulfur and thion- for those in which sulfur is substituted for the carbonyl oxygen. Somewhat different names have been suggested.^{104, 490} The term carbothionolic for the -CSSH group has been advocated.¹⁵²⁷

The free acids are unstable, though the trithio-carbonic can be isolated. The monothioacids and their salts are equilibrium mixtures and so are the alkoxy-esters and their salts:



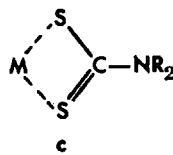
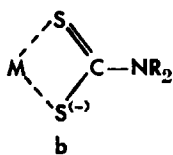
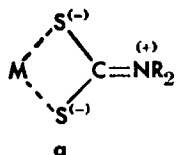
Ultra-violet absorption indicates that the ester-salt, EtO·CO·SK is in equilibrium with the EtO·CS·OK.^{717a, 720} The same must be true of the dithioacids and of their salts:



It is quite different when the hydrogens are replaced by alkyls. Well characterized esters of all six of the above acids, from carbonic to trithiocarbonic, are known. The esters, $\text{EtO}\cdot\text{CO}\cdot\text{SEt}$ and $\text{EtO}\cdot\text{CS}\cdot\text{OEt}$, can be made by methods which should give these structures and the esters so obtained differ from each other in physical properties and in reactions. The reactions of each correspond to the formula assigned. The same can be said of the isomeric esters: $\text{EtO}\cdot\text{CS}\cdot\text{SEt}$ and $\text{EtS}\cdot\text{CO}\cdot\text{SEt}$. The formulas for all of the thio-carbonic acids and for their ethyl esters were written out by Carius²⁵⁰ in 1859 and names were proposed for them by Bernthsen¹⁰⁴ in 1882.

The absorption spectra of the vapors of dithio- and trithio-carbonic esters have been considered as suggesting cyclic structures with double bonds between the two thiol sulfur atoms.¹³¹⁷ The absorption spectra of free trithio-carbonic acid and its ethyl ester in various organic solvents have been compared with that of its barium salt in water. The ester and acid have similar spectra.⁷⁰⁵ The long wave-length spectra of ethyl di- and trithio-carbonates have been compared with other compounds containing :C:O and :C:S .¹⁰⁸³

From absorption spectra studies, resonance structures a, b, and c, have been proposed for thiocarbamates and xanthates. Structure a, is of considerably smaller importance than b or c in xanthates, whereas in thiocarbamates all three resonance structures are important.



"M" refers to some metallic ion.^{275a, 923}

The mono-amides corresponding to these acids have not been isolated but it is useful to write them down since the amide-esters derived from them are important. They are:

1. $\text{H}_2\text{N}\cdot\text{CO}\cdot\text{OH}$
2. $\text{H}_2\text{N}\cdot\text{CO}\cdot\text{SH}$
3. $\text{H}_2\text{N}\cdot\text{CS}\cdot\text{OH}$
4. $\text{H}_2\text{N}\cdot\text{CS}\cdot\text{SH}$

The mono- and di-alkyl derivatives can be put with these:



For the mono-alkyl we can write the tautomeric forms:



The diamides are the well known urea and thiourea:



Both of these have tautomeric forms of which alkyl derivatives are known:



It is not necessary to write out the well known N-alkyl derivatives of these. The acid chlorides, which are useful in preparing many of the esters and amides, are phosgene and thiophosgene:



Half esters corresponding to these are:



Names for these were included in those proposed by Bernthsen. The reactions of the thiocarbonic acids and their derivatives have been reviewed by Tarbel and Harnish.¹⁵⁹²

Esters of Thiolcarbonic Acid, $\text{HO}\cdot\text{CO}\cdot\text{SH}$



BENDER'S SALTS, $\text{RO}\cdot\text{CO}\cdot\text{SM}$

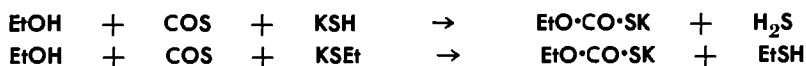
Esters of the first type are the most important. They are known only as their salts $\text{RO}\cdot\text{CO}\cdot\text{SK}$.

When carbon oxysulfide is passed into alcoholic potash an ester-salt is formed: ^{96, 1691}



This reaction was used to prove the identity of carbon oxysulfide from one source with that from another.^{1412a} Sodium cellulose reacts about two hundred times as rapidly with carbon oxysulfide as with carbon disulfide.⁷⁵⁵ At first sight it seems curious that in

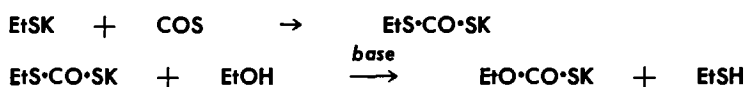
alcohol the same product is obtained when potassium hydrosulfide or mercaptide is substituted for the hydroxide:



It can be assumed that the first reaction is between the carbon oxydisulfide and the alcohol:



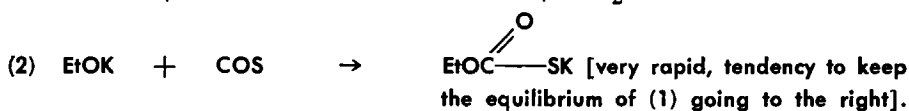
This is a strong acid that would displace hydrogen sulfide or mercaptan.^{786b} An alternate explanation of the formation of Bender's salt from a mercaptan is as follows:



This is by analogy with CS_2 which reacts as follows:



In the presence of the base RO^- readily replaces RS^- in many similar derivatives. Thus the true mechanism may be formation of a dithiolcarbonate followed by alcoholysis of the thio-ester linkage. With KSH and alcohol, the following equilibrium is probably involved:



This $\text{EtO}\cdot\text{CO}\cdot\text{SK}$ is the original Bender's salt; the name has been extended to other esters, $\text{RO}\cdot\text{CO}\cdot\text{SK}$. There is, of course, tautomerism:

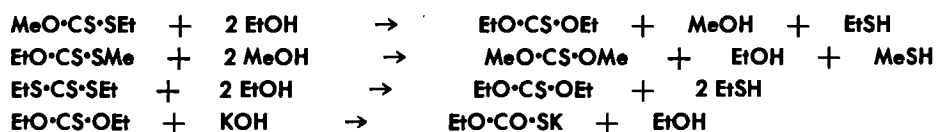


A Bender's salt may be obtained from thiophosgene and sodium ethylate:^{934a}



A Bender's salt can be prepared by partial saponification of the dithio- and trithio-esters, $\text{RO}\cdot\text{CS}\cdot\text{SR}$ and $\text{RS}\cdot\text{CS}\cdot\text{SR}$, by alcoholic

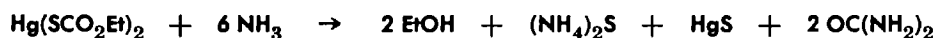
potash.^{401c, 568, 1450} The alkyl in the salt so obtained is derived from the alcohol which serves as solvent. This shows that alcoholysis precedes the saponification: ^{1412b, 1414}



It has been supposed that the alcoholate is added and that this complex is hydrolyzed.¹⁶⁷⁵ This is involved in the alcoholysis. A mercury salt results when ethyl formate, carbon disulfide, and mercuric oxide are heated in an atmosphere of nitrogen:



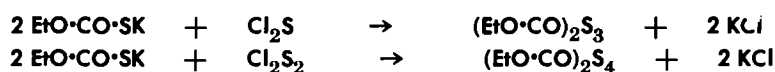
Ammonia causes ammonolysis, precipitating mercuric sulfide quantitatively: ⁵⁹⁰



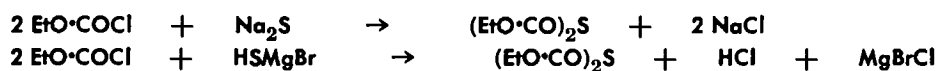
A Bender's salt can be estimated by titration with iodine: ¹⁶⁹¹



The product with a sulfur chloride is a polysulfide: ¹⁶³⁸



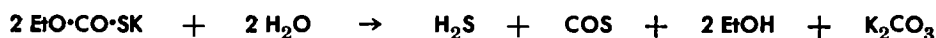
The thioanhydride results from the action of ethyl chloroformate on sodium sulfide ¹¹⁴⁰ or HSMgBr : ^{1160a}



The end product is the same with the trithiocarbonate: ^{786a}



A Bender's salt may be hydrolyzed: ⁹⁶



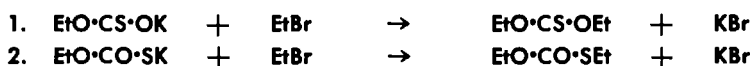
Pyrolysis takes place at 170° : ⁹⁶



Alkylation is readily effected: ^{1412b}

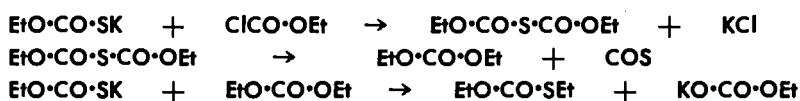


The fact that the alkyl in this ester is joined to sulfur does not prove that all of the ester-salt is in the form of $\text{EtO}\cdot\text{CO}\cdot\text{SK}$. Attention has been called several times to the rapidity of the reaction of an alkyl halide with a metal joined to sulfur as contrasted with the corresponding oxygen compound. We can write the two reactions:



Since the second reaction is the fast one and since the equilibrium is quickly reestablished, the ester $\text{EtO}\cdot\text{CO}\cdot\text{SEt}$ will be the chief product.

The potassium salt reacts with ethyl chloroformate to give carbon oxysulfide, carbon dioxide, ethyl carbonate, and ethyl thiolcarbonate.¹⁷¹³ It is easy to account for the ethyl carbonate but not for the thiol- unless it is produced by alkylation of the original salt:



Bender's salt can replace ammonium thiocarbamate, H_2S or even $(\text{NH}_4)_2\text{S}$ in analysis.⁵⁴⁵ Compounds, said to be useful in flotation, are obtained by reacting an acid chloride such as benzoyl chloride with a salt of a monothioacid such as potassium ethyl monothio-carbonate.^{902b, 1158d} The disulfide, $(\text{EtO}\cdot\text{CO}\cdot\text{S})_2$, is said to be useful in vulcanization.⁸⁵

ESTER-SALTS, $\text{RS}\cdot\text{CO}\cdot\text{OK}$

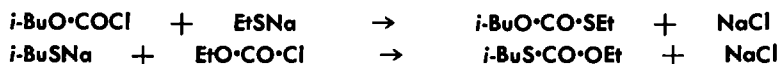
Little is known of these which are isomeric with Bender's salts. Carbon dioxide reacts with potassium mercaptide:



The product was supposed to be identical with Bender's salt but this does not seem likely.^{271b} This reaction should be investigated. An ester-salt of this type will probably have little stability. As the metal is not in combination with sulfur it will not be very reactive.

The neutral esters, $\text{RO}\cdot\text{CO}\cdot\text{SR}'$, can be obtained by alkylating Bender's salts as indicated above. They can also be made either

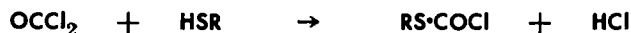
from chloroformic esters and mercaptides^{1203b} or from chlorothioformic esters and alcoholates: 186, 599, 1203b, 1413a



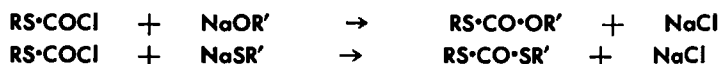
A Grignard reagent reacts with a chloroformic ester to form a thiolcarbonate: 598, 750



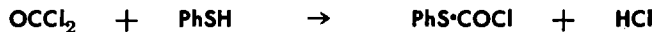
Analogous reactions have been carried out with *i*-amyl compounds in place of *i*-butyl.^{1462a, 1462b} Sodium is added to a solution of the mercaptan in dry ether and then the chloroformate is put in. Phosgene reacts slowly with a mercaptan: 38, 1413a, 1462a, 1462b



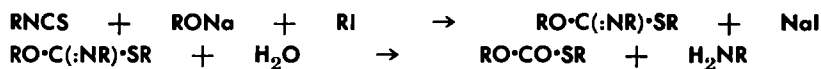
The second chlorine is brought into reaction by alkali: 1412b, 1413a



With thioglycolic acid phosgene forms the cyclic thiolcarbonate 1,3-oxathiolan-2,5-dione.³⁹⁵ Thiophenol reacts with phosgene in toluene solution: 498, 1365b

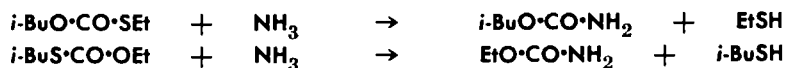


From this chloride the ethyl ester, $\text{PhS}\cdot\text{CO}\cdot\text{OEt}$, and the phenyl ester, $\text{PhS}\cdot\text{CO}\cdot\text{OPh}$, have been prepared.^{1365b} These esters can be made by the hydrolysis of the imido-esters which result from the action of sodium alcoholate and an alkyl iodide on a mustard oil: 410b, 622



The cyclic resorcin aminothiocarbonate, heated with dilute acid, gives a nitrogen-free thiocarbonate.⁸⁸⁶ Monothiocarbonates of aromatic polyhydroxy compounds are recommended as azo dye intermediates and disinfecting agents.^{1708b}

Hydrolysis of thiolcarbonic esters is catalyzed by bases.^{675, 1257, 1564} Oxidation of an aryl thiolcarbonate may yield an aryl sulfonic acid.¹²⁵⁷ Ammonia displaces the mercaptan rather than the alcohol: 417, 1413a



Cyclic thiocarbonates react with ammonia or an amine to give thiocarbamates.¹²⁵⁸

Thionesters, $\text{RO}\cdot\text{CS}\cdot\text{OR}$

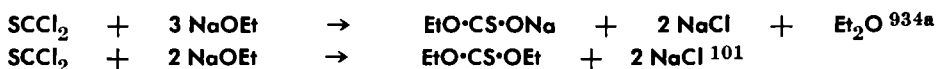
Esters of this type are not well known. Thiophosgene reacts with an alcohol in two ways:^{52, 934a}



This chloride reacts with sodium alcoholate suspended in ether:^{101, 410b, 411a, 1366}



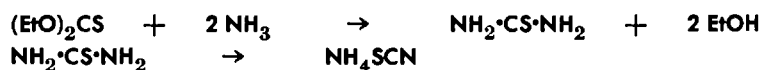
Thiophosgene has been found to react with sodium ethylate in two other ways:



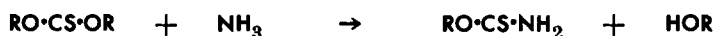
The ester, $(\text{EtO})_2\text{CS}$, has been obtained by distilling potassium ethyl xanthate.^{401c} The diphenyl ester, $(\text{PhO})_2\text{CS}$, is from sodium phenate and thiophosgene.^{52, 101, 1318} Sodium phenate and thiophosgene give the chloride, $\text{PhO}\cdot\text{CS}\cdot\text{Cl}$, from which $\text{PhO}\cdot\text{CS}\cdot\text{OEt}$, $\text{PhO}\cdot\text{CS}\cdot\text{SPh}$, $\text{PhO}\cdot\text{CS}\cdot\text{NH}_2$, $\text{PhO}\cdot\text{CS}\cdot\text{NHPh}$, and $\text{PhO}\cdot\text{CS}\cdot\text{NMe}_2$ have been prepared.^{1365a, 1366} The formation of thionesters is considered further under xanthates.

The phenyl ester, $(\text{PhO})_2\text{CS}$, rearranges to $\text{PhO}\cdot\text{CO}\cdot\text{SPh}$ when it is heated to $280\text{--}300^\circ$.^{1460a, 1461} This does not seem to have been tried with the alkyl esters. Excess of alkali in dilute alcohol solution converts it to phenyl disulfide.¹⁴⁶¹ This is a case of saponification followed by air oxidation of the sodium thiophenate. This is known as the Schönberg rearrangement. Its mechanism and kinetics have been discussed.^{18, 1310}

It was noted above that the mercapto group, RS- , is more readily replaced than the alkoxy-, RO- . At 100° with an excess of alcoholic ammonia both RO- groups are removed and diethyl thioncarbonate is converted to ammonium thiocyanate. Thiourea must be the intermediate:



With aniline, instead of ammonia, the product is diphenylthiocarbanilide, $\text{PhNH}\cdot\text{CS}\cdot\text{NHPh}$, which cannot rearrange.⁴¹⁷ Ammonia, in limited amounts, displaces one of the alkyls to give the thiourethane: ⁴¹⁷



The sulfur in diphenyl thioncarbonate is replaced by oxygen when it reacts with heavy metal salts⁶¹⁰ or oxides: ¹⁴⁶¹



The chlorides, $\text{RO}\cdot\text{CSCl}$, have been used for making esters of thion acids: ^{410b, 411a}



Thiophosgene reacts slowly with cold water. The same can be said of the chlorides $\text{RO}\cdot\text{CSCl}$.

The decomposition of the chloride, $\text{EtO}\cdot\text{CSCl}$ is unaffected by light but is accelerated by dimethylaniline.¹⁰⁸ A comparison of the thiochloroformates with the chloroformates has been made. The minimum decomposition temperatures in the presence of quinoline are in Table 1.2.²⁵³

TABLE 1.2

Minimum Decomposition Temperatures

<i>R</i>	<i>RO</i> · <i>CSCl</i>	<i>RO</i> · <i>COCl</i>	<i>R</i>	<i>RO</i> · <i>CSCl</i>	<i>RO</i> · <i>COCl</i>
Methyl	19	36	Octyl	65	67
Ethyl	39.5	59	Nonyl	58	73
Propyl	29	66	Decyl	61	68
Butyl	55.5	81	Undecyl	60	76
Amyl	50	72	Allyl	18	37
Hexyl	67	87	$\text{ClCH}_2\text{CH}_2-$	45	50
Heptyl	58	78	$\text{PhCH}_2\text{CH}_2-$	55	66

Dithiocarbonic Acids, Salts, and Esters

These have been reviewed.¹⁷⁰⁸ The salts, $\text{RO}\cdot\text{CS}\cdot\text{SK}$, are known as xanthates. They are interesting historically and important technically.

XANTHATES

History

Organic sulfur chemistry began with xanthates and with Zeise, who worked with them before he got around to the mercaptans. His earliest publication on them in 1815 was followed by a number of others in Danish journals.^{1789a}

He dissolved sodium or potassium in alcohol, added carbon disulfide and got crystals which he recognized as salts of a new acid. The potassium salt is soluble in water and in alcohol but insoluble in ether. He made copper, lead, mercury, and zinc salts and the free acid which reacted with iodine to give an oil. The acid decomposed readily setting free carbon disulfide. He called it xanthogen, or "yellow former" from the Greek xanthos, yellow, on account of the color of the copper precipitate.^{1789a} He determined the formula, $\text{KS}_4\text{C}_6\text{H}_{10}\text{O}_2$, using old atomic weights, one atom of potassium, two molecules of carbon disulfide, and one of ether. However, he was unable to get the xanthate from ether.^{1789c, 1789d} He analyzed potassium, sodium, barium, lead, and copper xanthates. The barium salt was from barium oxide and an alcoholic solution of carbon disulfide.^{1790a}

Apparently without any knowledge of Zeise's publications, Couerbe^{339a, 339b} prepared potassium and lead xanthates. His inadequate reading was called to his attention by Zeise;^{1790b} Pelouze and Liebig asked why Frenchmen did not read German.¹²⁷⁷ Couerbe gave full credit to Zeise and added full directions for making potassium xanthate from the hydroxide.^{339c}

Zeise added iodine to potassium xanthate:



The product was a liquid insoluble in water.^{1790d} This disulfide was prepared in the same way by Desains,⁴²⁹ and later by Debus using chlorine.^{401d} Zeise turned his attention to methanol, making the xanthic salts and the disulfide, $(\text{MeO} \cdot \text{CS} \cdot \text{S})_2$.¹⁷⁹¹ Dumas and Peligot had previously prepared potassium methyl xanthate and compared xanthates to carbonates.⁴⁷⁶ Cetyl alcohol was dissolved in carbon disulfide and potassium hydroxide added. A voluminous salt was obtained from which the zinc and barium xanthates were prepared.¹³¹¹ *i*-Amyl alcohol was xanthated,^{62, 506, 868, 1445, 1803a} so also were propyl^{271c, 1376} and *i*-butyl.^{1203a}

The Preparation of Xanthates

The rate of formation of potassium xanthate has been measured and the reaction has been found to be bimolecular.^{642, 1182} The xanthation of cellulose fibers is also bimolecular.⁷⁵⁵ The conditions of formation of xanthates have been studied.¹⁶³¹ By use of sodium hydroxide containing O^{18} it was shown that this is the oxygen atom that goes to make the water; the oxygen of the alcohol goes into the xanthate:



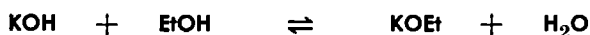
There is no exchange of oxygen between water and alcohol or cellulose or between water and the xanthate of an alcohol or of cellulose.¹⁹⁰ This conclusion was reached by Zeise more than a century earlier.^{1789c} The kinetics of the exchange of sulfur in xanthates has been studied with the aid of labeled sulfur.^{555, 1147}

The xanthate reaction is strictly between a metal alcoholate and carbon disulfide:

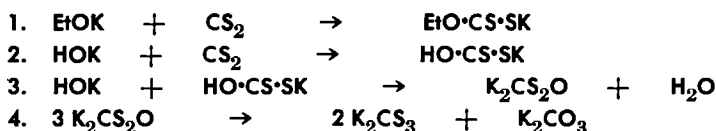


As stated above the original method was to dissolve sodium or potassium in absolute alcohol and add the carbon disulfide. In this case there was excess alcohol, which may have helped or hindered, but the reaction took place satisfactorily.

When potassium hydroxide is added to a mixture of water and alcohol there is an equilibrium:



Carbon disulfide can react with either the hydroxide or the alcoholate:



We know that carbon disulfide dissolves in potassium hydroxide solution and that potassium trithiocarbonate is one of the final products, so can assume that reactions 2 and 3 must take place. Reaction 1 is favored over 2 since when carbon disulfide is shaken with 5% ethyl alcohol in aqueous alkali, 44% of it is converted to the xanthate. With 15% alcohol the yield of

xanthate is 60%.^{790c} It is general practice to bring together a concentrated aqueous solution of potassium or sodium hydroxide with somewhat more than the calculated amount of alcohol and carbon disulfide.¹³⁸⁴ Couerbe used solid caustic potash, absolute alcohol, and carbon disulfide in the ratio 1:1.75:1.11 equivalents.^{339c} Sacc saturated absolute alcohol with potassium hydroxide and added an excess of carbon disulfide. The excess of alcohol was evaporated below 50° or the xanthate was precipitated by adding ether.¹⁴⁰⁶ A concentrated alcoholic solution of potassium hydroxide and carbon disulfide give a nearly quantitative yield.⁸⁶² A mixture of alcohol and carbon disulfide may react with a dry metal hydroxide, all in molecular proportions.¹¹⁶⁴ The alcohol and alkali may be mixed and the carbon disulfide added slowly, keeping the temperature below 50°. ⁷⁰ According to another patent the temperature is kept below 35°. ^{771a} The alcohol and carbon disulfide are mixed and sodium hydroxide added slowly.²⁹⁴ Or carbon disulfide is added to a mixture of alcohol and potassium hydroxide at such a rate that the temperature does not rise above 35°. The smallest possible excess of alkali and alcohol is best, 1.1 of each to 1 of carbon disulfide.⁹¹⁷ Xanthates can be prepared similarly from the higher alcohols. Primary alcohols react well, secondary less so and tertiary only at high temperatures with poor yields.⁹¹⁸ Operating methods have been given.⁵⁴⁰ The carbon disulfide may be added to the mixture of caustic alkali and alcohol as a vapor.^{574, 1745} The caustic alkali is dispersed in the alcohol and the carbon disulfide added at a suitable temperature.^{954, 1386} Commercial carbon disulfide is mixed with butyl alcohol and alkali added.¹⁰³⁴ The higher alcohols have been xanthated ^{564, 948} up to cetyl ⁷⁵¹ and octadecyl.¹²⁷ A solution of a ready formed xanthate is mixed with the alcohol and alkali before adding the carbon disulfide.^{771c} The xanthates from the lower alcohols are very soluble in water. After they are formed additional sodium or potassium hydroxide may be added to salt them out so as to increase the yield.^{770d, 771b, 1444} Getting rid of water, whether that originally present in the mixture or that formed in the reaction aids in completing the reaction and in the recovery of the water-soluble xanthate. The reaction may be conducted at a reduced pressure so that evaporation is favored ^{1237b, 1387, 1388c} or an inert volatile liquid may be added to form an azeotrope with the water.^{1237d} Anhydrous salts may take

up the water that is formed in the reaction.⁷⁷² The reaction may be carried out in an inert medium such as a liquid hydrocarbon.³⁶⁷ Carbon tetrachloride and other chlorinated hydrocarbons are said to be catalysts enabling the reaction to go at 10°. ^{770c}

Alkali metal alcoholates are prepared especially for xanthation.¹¹²³ The use of dry sodium alcoholates is desirable ¹⁰³⁹ even with the lower alcohols such as ethyl and butyl, since with them the yields are more nearly quantitative and the temperature may be allowed to go as high as 80°. For preparing xanthates from secondary and tertiary alcohols it is particularly desirable to use alcoholates free from water.^{771d, 1237a}

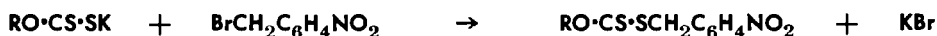
A tertiary alcohol may be mixed with finely ground potassium hydroxide or have sodium dissolved in it. A secondary alcohol may be mixed with 50% aqueous potassium hydroxide.^{1388a} Menthol and borneol may be made to react with sodium and the products converted to xanthates.⁶⁴ Their absorption spectra ^{301b, 1631} and rotatory dispersion ¹⁰⁵⁴ have been measured. A terpene alcohol such as terpineol may be xanthated in this way.¹³³⁰ The terpineol may be heated with sodium at 170° to produce the sodium terpineolate.⁴⁸⁶

Carbon disulfide can be caused to react with an alkylene glycol, glycol ester, or an alkylene oxide and alkali.^{1237c} Various polyalcohols have been xanthated.⁵⁵ Highly substituted hydroxyindene derivatives react with sodium and carbon disulfide to form xanthates.^{727d} A xanthate can be prepared from glycogen but there is degradation in the process.¹⁵⁵⁴ Only mono-xanthates have been obtained from glycerol,^{1021, 1039, 1327c} glucose ^{1021, 1022} and other polyalcohols.¹⁰²¹ Dextrin yields a xanthate from which plastic masses can be obtained.¹⁵⁰³ Polyvinyl alcohol yields a solution similar to viscose.¹⁵⁴² Xanthates can be made from unsaturated alcohols ^{671, 672, 740, 936} and from resin alcohols.^{125a} Metal xanthates of haloaryloxyalkanols have been patented.^{461, 462, 541}

An alkylmercuric hydroxide may take the place of the alkali though a trace of sodium hydroxide must be present. The products melt at moderate temperatures.⁹⁵⁷ Tetramethyl ammonium hydroxide and triethylsulfonium hydroxide in alcohol with carbon disulfide give xanthate reactions.⁵³³ Guanidine carbonate reacts with a mixture of carbon disulfide and an alcohol.⁸⁴⁷

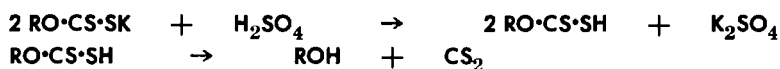
The formation of xanthate may be used to free benzene of carbon disulfide.⁶⁷⁴

Xanthates may serve for the identification of alcohols. Powdered potassium hydroxide is dissolved in the alcohol by heating. Ether and carbon disulfide are added with stirring. More ether is added and the xanthate is filtered off. It is purified by dissolving in water or acetone and precipitated with ether. From an iodine titration the molecular weight of the alcohol is deduced.¹⁷²⁸ The potassium xanthates of twelve common alcohols can be titrated with perchloric acid in glacial acetic acid.¹⁰⁰ In addition to the titrations the melting points of the xanthates, $\text{RO}\cdot\text{CS}\cdot\text{SK}$, may be taken. These are mostly high and not sharp but are of service.¹⁴⁹³ Some are given in the lists of physical properties. Identification of these derivatives has been achieved also with the aid of chromatography, crystallography, potentiometric titrations, and eutectic temperatures.^{35, 248, 1546, 1683} Derivatives having distinctive melting points should result from the reaction of the xanthates with a halide such as *p*-nitrobenzyl or *p*-bromophenacyl bromide:



Free Xanthic Acids

When cold dilute sulfuric acid is added to a cold concentrated solution of a xanthate the free acid is precipitated as a pale yellow, unstable oil: ^{116, 506, 1243}



The solubility of the methyl acid, $\text{MeO}\cdot\text{CS}\cdot\text{SH}$, in water is 5.4 g. per liter at 0° and that of the ethyl 2.4 g. The dissociation constants for these acids are 0.034 and 0.030.⁷⁰³ On account of their rapid decomposition the value of *K* was found by extrapolation to be 0.028 for the ethyl.⁷¹⁸ The benzyl acid, $\text{PhCH}_2\text{O}\cdot\text{CS}\cdot\text{SH}$, melts at 29° and can be kept for several hours.⁷⁰³ The ethyl acid melts at about -53° .⁷⁰⁴ The corresponding selenium acid, $\text{EtO}\cdot\text{CO}\cdot\text{SeH}$, melts at 123° .^{1160b}

The decomposition of the ethyl acid at 0° has been studied extensively ^{274, 703, 704, 925, 1555} and found to be monomolecular.⁷⁰⁴ The rate of decomposition depends to a remarkable degree on the solvent.⁷⁰³

TABLE 2.2
Rate of Decomposition of Xanthic Acid

In carbon disulfide	1	In nitrobenzene	315
hexane	1.5	ether	485
chloroform	3.6	acetone	26,000
benzene	5.2	ethanol	1,000,000

In hydrocarbons it is low; in oxygenated solvents it is rapid, particularly so in alcohol. In a hydrocarbon the decomposition is autocatalytic, due to the liberated alcohol.⁷⁰⁴ The temperature coefficient is unusually high, 6.75 for 10°. ⁹²⁵ The kinetics of the decomposition of propyl xanthic acid has also been studied.¹⁴⁵⁸

The aminolysis of ethylxanthogenacetic acid has been studied.¹⁰⁹⁹

The xanthic acid from borneol, $C_{10}H_{17}O \cdot CS \cdot SH$, is levorotatory; the dispersion is abnormal, reaching a maximum at $\lambda = 525\mu$ and then decreasing rapidly.^{298d}

Salts of Xanthic Acids

The potassium and sodium salts are the ones that are obtained directly in the usual methods of preparing xanthates yet little is ever said about their properties. They are insoluble in ether and hydrocarbons. Those from the lower alcohols, at least, are quite soluble in water and only slightly so in alcohol. The densities of several have been determined: $MeO \cdot CS \cdot SK$, 1.7002 at 15.2°, $EtO \cdot CS \cdot SK$, 1.558 at 21°, $i-BuO \cdot CS \cdot SK$, 1.3718 at 15°. ³⁰⁷ The addition of a basic compound such as lime is said to stabilize a xanthate.⁷¹ Impurities such as carbonates, thiocarbonates, and sulfides can be eliminated by the addition of just the right amount of sulfuric acid.^{770a} Alkali metal xanthates of amyl alcohol have been prepared.⁴³¹

The preparation of xanthates of the heavy metals is a simple matter: an aqueous solution of a salt, such as copper sulfate, is added to a neutral solution of a potassium or sodium xanthate and the precipitate is filtered off. Zeise and the other early experimenters ^{476, 773b, 1789a, 1790a} did this using such water soluble salts of the heavy metals as were at hand with the xanthates

from ethyl and methyl alcohols. By 1862 nickel, cobalt, chromium, iron, mercury, tin, bismuth, antimony, and arsenic xanthates had been prepared. Copper and zinc may be separated by use of the xanthates.^{1701b} Many other alcohols have been xanthated and the corresponding heavy metal salts prepared by later investigators.^{47a, 470b, 1092b, 1092c, 1093c} The precipitates usually give the expected analytical figures and there is little to say about them. The solubilities in water of the heavy metal xanthates are very low. They increase in this order: zinc, nickel, cadmium, thallium, lead, arsenious, cobaltic, cuprous, silver, and mercuric.^{1093c} Another author gives the reverse order; mercuric, mercurous, auric, silver, cuprous, bismuth, lead, cadmium, nickel, ferrous, zinc. The solubility product for $\text{AgS} \cdot \text{CS} \cdot \text{OEt}$ is 3.5×10^{-17} .¹²⁹¹ The following form water insoluble ethyl xanthates: Zn^{++} , Fe^{+++} , Ni^{++} , V^{+5} , CO^{++} , Sn^{++} , Sb^{+++} , Sn^{+4} , Bi^{+++} , Cd^{++} , Pb^{++} , UO_2^{++} , Hg^{++} , Cu^{++} , and Ag^+ . Of these Cu, Ag, Cd, Hg, and UO_2 xanthates are not extractable by organic solvents.¹²⁹³

The yellow color of ethyl copper xanthate suggested to Zeise the name for the group. The precipitate as obtained has the composition of the cupric salt, $(\text{RO} \cdot \text{CS} \cdot \text{S})_2\text{Cu}$, but Zeise and Debus^{401a, 401c} recognized it as the cuprous salt mixed with dixanthogen and wrote the correct equation for its formation:



The dixanthogen may be dissolved out by an organic solvent.^{1327a, 1327b, 1327c} It is curious that cupric xanthate is not infrequently mentioned in chemical literature a century after its existence was disproved.^{114a, 1126a} The dark color of the copper xanthate when first precipitated has been attributed to the presence of copper trithiocarbonate^{1327a, 1327b, 1327c} and to its amorphous state.⁴⁴⁰ The formation of cuprous xanthate is used for the detection and determination of carbon disulfide and of copper. Water in a copper vessel may respond to this test.⁵³⁹ Cuprous *i*-butyl xanthate is only slightly soluble in cold organic solvents but more so in hot chloroform, carbon disulfide, or benzene.⁴⁴⁰ Cuprous allyl xanthate is readily prepared.¹²⁴³ The formation of a copper salt has been cited as proof that a xanthate was formed.¹⁰²¹

Silver xanthates are formed by the usual precipitation method^{401a, 401c, 1243} or by leaving silver chloride, bromide, or

iodide in contact with potassium xanthate solution. Silver xanthate is not affected by dilute acids even at 100° .¹³⁴³

Lead xanthate was prepared and its formula determined in 1838.^{339b, 401a, 401c} It is decomposed by mineral acids and even by boiling water. Iodine converts it to dixanthogen.^{401a, 401c} The mercurous salts are normal, the mercuric are basic.¹¹⁷⁸

The crystal structure of cobaltous xanthate, $(\text{EtO}\cdot\text{CS}\cdot\text{S})_2\text{Co}$, d. 1.63, has been determined;⁴²⁵ so has that of the nickel salt.¹⁵¹ The cobaltic salt melts at 117° .^{470a} Pyridine forms addition compounds with cobalt and nickel xanthates containing various alkyls: ethyl, propyl, butyl, amyl, bornyl, cyclohexyl, and cetyl. The nickel salt, $(\text{EtO}\cdot\text{CS}\cdot\text{S})_2\text{Ni}$, takes up six molecules of ammonia.^{470b} Nickel and cobalt xanthates have been prepared starting with methyl, ethyl, propyl, butyl, *i*-butyl, *s*-butyl, and *i*-amyl alcohols and their absorption spectra determined.⁴¹⁶

The crystal structure of ferric xanthate has been determined.^{402, 470a} When ferrous sulfate in 50% alcohol is saturated with nitric oxide and potassium xanthate is added, dinitrosoferrous xanthate, $\text{Fe}(\text{NO})_2(\text{S}\cdot\text{CS}\cdot\text{OEt})_2$, is formed.¹¹⁰⁰ The same salt is obtained by passing nitric oxide into ferric xanthate.²³⁷

The methods of preparing zinc salts from xanthates from ethyl and higher alcohols are given in patents.^{188, 358} The xanthates of selenium (II) and tellurium (II) have been prepared.^{561a, 561c}

Platinum xanthate, $(\text{EtO}\cdot\text{CS}\cdot\text{S})_2\text{Pt}$, has been described. It takes up two molecules of ammonia.¹³²⁹

A gold salt is made by adding dropwise a 10% solution of auric chloride to a 25% solution of a xanthate, $\text{RO}\cdot\text{CS}\cdot\text{SK}$, in three fold excess. The aurous salt is precipitated.^{423b} The melting points of the salts, $\text{RO}\cdot\text{CS}\cdot\text{SAu}$, are given in the lists of properties.

A reaction between molybdic acid and potassium ethyl xanthate has been observed¹⁴⁹⁹ and a method for detecting this metal founded on it.⁸⁹² Potassium methyl xanthate is used in a spot test for molybdenum in steel analysis.¹⁶⁰² Molybdenum xanthate is insoluble in most solvents but is soluble in carbon disulfide and in carbon tetrachloride.²⁶³ It has the composition $(\text{EtO}\cdot\text{CS}\cdot\text{S})_4\cdot\text{Mo}_2\text{O}_3$. The corresponding *i*-butyl and *i*-amyl salts are known.¹¹⁷³ The ethyl molybdenum xanthate, the propyl, the butyl, the *i*-butyl, the *i*-amyl, and the cyclohexyl have been prepared. The methyl decomposes without melting.^{1092b} The uranium salts have the general formula $\text{UO}_2(\text{S}\cdot\text{CS}\cdot\text{OR})_2$ and are readily hydrolyzed.

The ethyl, *i*-amyl, *i*-propyl, propyl, butyl, *i*-butyl, and cyclohexyl compounds have been prepared.^{1092b} The reaction of uranyl ion with xanthates has been described.¹⁸⁰¹

Powdered potassium xanthate suspended in toluene is mixed with arsenious chloride and acetic acid added. The precipitate is $(\text{EtO}\cdot\text{CS}\cdot\text{S})_3\text{As}$, insoluble in water, somewhat soluble in hot alcohol, soluble in benzene, carbon disulfide, and ether.¹⁵⁹³ Or hydrochloric acid is added to a solution of sodium arsenite and potassium xanthate.^{1092c} Carbon disulfide may be estimated by adding it to potassium arsenite in alcohol.¹⁵⁹³ Arsenious xanthate is rhombohedral.¹⁵² The corresponding antimony compound, $(\text{EtO}\cdot\text{CS}\cdot\text{S})_3\text{Sb}$, is also rhombohedral.⁴²⁶

Complex alcohols such as the cellosolves and carbitols can be xanthated. The copper salts from these are said to be useful as fungicides.²⁵⁴ Alkyl- or aryl-tin alkyl xanthates show marked stabilizing properties for vinyl chloride-acetate copolymers.³⁶

Reactions of Xanthates

The oxidation by cupric ion, which has been considered in the section on salts, was one of the first xanthate reactions to be discovered. The oxidation by iodine was an early discovery.^{227, 401a, 868, 957, 1790d} Chlorine may be used instead of iodine: ^{3, 331b, 430d, 453, 1203a, 1393}



Electrolysis effects the same oxidation.^{770b, 1428, 1429} Ammonium⁵²⁹ or potassium persulfate,^{823, 1167} cyanogen bromide²⁴¹ or chloride,^{459b} chlorite,²⁷⁹ hypochlorous acid,^{200a, 520, 862} and oxides of nitrogen, with or without added oxygen, are recommended as oxidation agents.^{817a, 1795a} Chloramine-T,^{213b} sodium tetrathionate, $\text{Na}_2\text{S}_4\text{O}_6$,²⁴¹ nitrous acid,^{241, 1795b} nitrosyl chloride, and *p*-toluene sulfone amide and chloride²⁴¹ convert xanthates to disulfides.

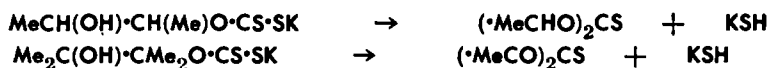
Hydrogen peroxide converts the $-\text{CS}-$ group into carbonyl, $-\text{CO}-$.^{864, 932a, 932b} Oxidation in aqueous potassium hydroxide solution by hydrogen peroxide has been used as a method of determining sulfur¹²⁸⁰ in potassium xanthate and in dioxanthogen.

In aqueous solution potassium xanthate is slowly hydrolyzed. The final product is potassium trithiocarbonate. With excess

alkali potassium sulfide and carbonate are formed.^{388, 401c, 935} The conductivity of the salts, $\text{EtO}\cdot\text{CS}\cdot\text{SK}$, $\text{EtO}\cdot\text{CS}\cdot\text{SNa}$, $\text{BuO}\cdot\text{CS}\cdot\text{SK}$, and $\text{AmO}\cdot\text{CS}\cdot\text{SK}$, indicates complete dissociation in the concentrations used in flotation. The collecting action in flotation is due to ionic adsorption.¹⁴³⁰

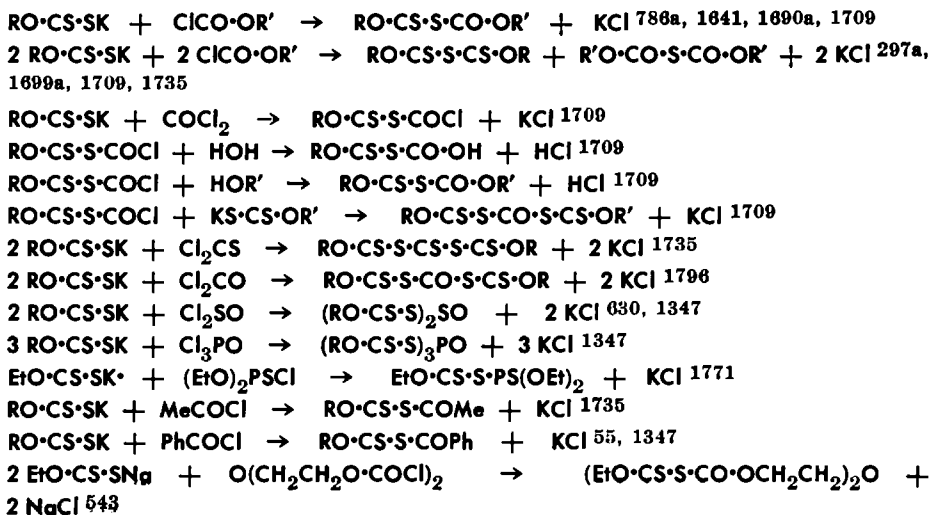
A variety of products have been reported as formed by the pyrolysis of potassium ethyl xanthate: mercaptan, carbon disulfide, and liquids boiling at 130° and at $140\text{--}5^\circ$; ^{339d} alcohol, mercaptan, carbon disulfide, hydrogen sulfide, and carbon dioxide; ¹⁴⁰⁶ carbon disulfide, ethyl sulfide and disulfide, and carbon oxysulfide; ⁵⁴⁸ hydrogen sulfide, carbon dioxide, disulfide and oxysulfide, alcohol, mercaptan, ethyl sulfide, and disulfide.⁷⁴¹ The residue is potassium sulfide, sulfite, thiosulfate, and carbonate. Nickel and silver xanthates give good yields of the diethyl ester, $\text{EtO}\cdot\text{CS}\cdot\text{SEt}$.⁷⁴¹ The *i*-butyl compound gives *i*-butyl sulfide, potassium sulfide, and carbon monoxide.^{1203a}

The mono-xanthates, of 2,3-butylene and 2,3-diamethylbutylene glycols, on heating, rearrange to the cyclic thion carbonates: ^{556, 1563}

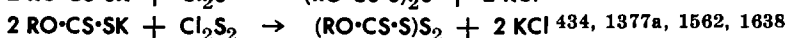


Heating resorcinol or pyrogallol with potassium xanthate forms an aryl dithioacid salt.¹⁰³³

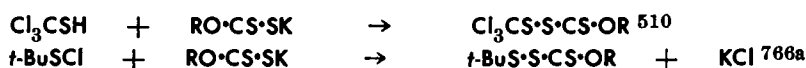
With acid chlorides mixed anhydrides are produced:



Sulfur chlorides give xanthyl polysulfides:

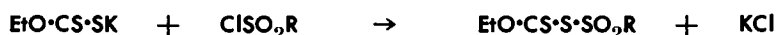


With a mercaptan or an alkylsulfenylhalide a disulfide is formed:



The trichloromethyl disulfides have fungicidal properties.⁵¹⁰

The initial reaction of a xanthate with a sulfonyl chloride is the formation of an unstable thioanhydride:

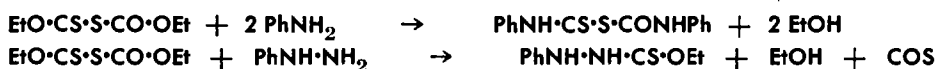


According to conditions, this decomposes in various ways, one of which is:



The xanthic ester $\text{EtO} \cdot \text{CS} \cdot \text{SEt}$ may be formed.^{213c, 213d}

The reaction of ethyl chloroformate with potassium xanthate gives the thioanhydrides $\text{EtO} \cdot \text{CS} \cdot \text{S} \cdot \text{CS} \cdot \text{OEt}$ and $\text{EtO} \cdot \text{CS} \cdot \text{S} \cdot \text{CO} \cdot \text{OEt}$.^{786a, 1699b} The compound $\text{EtO} \cdot \text{CO} \cdot \text{S} \cdot \text{CS} \cdot \text{OPr}$ is a liquid while $\text{PhMeN} \cdot \text{CS} \cdot \text{S} \cdot \text{CS} \cdot \text{OPr}$ melts at 42° .²³⁹ The thionhydride reacts with aniline and with phenylhydrazine.⁶⁸² With aniline different products are reported:



Another author found the product with aniline to be a thioncarbamate:¹⁴²²



It is claimed that thioanhydrides can be produced by treating thiocarbamates with cyanogen chloride.^{1309b, 1540a, 1540b, 1540c} The product with phosgene decomposes to give a high yield of the thioanhydride:

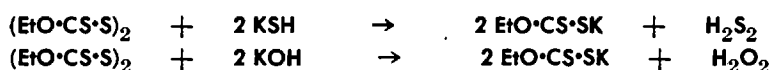


The mixed thioanhydrides, $\text{RO} \cdot \text{CS} \cdot \text{S} \cdot \text{CO} \cdot \text{OR}'$, have been claimed as parasitocides^{1652, 1709} and flotation agents,^{459b, 542, 543, 680} the xanthic anhydrides, $\text{RO} \cdot \text{CS} \cdot \text{S} \cdot \text{CS} \cdot \text{OR}$,⁶⁸⁰ as flotation agents,⁶⁷⁹

accelerators,^{129c, 1309a, 1721c} and insecticides,¹⁷⁹⁶ and the xanthic polysulfides,^{1720b} $(\text{RO}\cdot\text{CS})\text{S}_3$ ^{1377a} and $(\text{RO}\cdot\text{CS}\cdot)_2\text{S}_4$,^{1377a, 1548, 1562} as accelerators, antioxidants, and corrosion inhibitors for lubricating oils. Bis(ethoxythiocarbonyl) tetrasulfide is used as an additive in high pressure lubricants.^{434, 1146} The carbonyl and sulfonyl compounds, $(\text{RO}\cdot\text{CS})_2\text{CO}$ and $(\text{RO}\cdot\text{CS})_2\text{SO}_2$, are aids to flotation.⁵⁴² Addition of a xanthic sulfide, $(\text{RO}\cdot\text{CS})_2\text{S}$, to Thiokol decreases flow resistance.^{130b} A xanthic polysulfide, $(\text{ROCS})_2\text{S}_4$, in a cutting oil increases loading weights.¹⁷⁹⁹ An ammonium salt, ROCS_2NH_4 , reacts with two molecules of formaldehyde to give the salt $\text{ROCS}_2\text{N}(\text{:CH}_2)_2$.^{1006d}

Dixanthogens, $(\text{RO}\cdot\text{CS}\cdot\text{S}\cdot)_2$

The methyl, ethyl, *i*-amyl, and cetyl compounds were prepared by Desains by the action of iodine on the corresponding xanthates. They were subjected to the action of ammonia and of heat.⁴²⁹ Menthyl potassium xanthate reacted similarly with iodine.^{297a, 298c} When dixanthogen is heated ethyl thioncarbonate, $(\text{EtO})_2\text{CS}$, and ethyl xanthate, $\text{EtO}\cdot\text{CS}\cdot\text{SEt}$, are formed. With potassium hydroxide the products are potassium xanthate and carbonate and sulfur. With potassium hydrosulfide they are potassium xanthate, mercaptan, hydrogen sulfide, and sulfur.^{401a, 401c, 401d, 586} The reaction has been written:

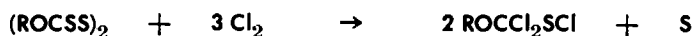


The hydrogen disulfide decomposes into hydrogen sulfide and sulfur while the hydrogen peroxide oxidises some of the xanthate.⁴⁶⁶ This should not be taken to mean that hydrogen peroxide is actually produced. Dixanthogen is produced by the oxidation of the xanthic ion and acts as an oxidising agent when it returns to the ion. With sodium the xanthate is produced: ⁴⁶⁶



With ammonia a xanthogen amide, $\text{RO}\cdot\text{CS}\cdot\text{NH}_2$, is one of the products from a dixanthogen, $(\text{RO}\cdot\text{CS}\cdot\text{S}\cdot)_2$.^{241, 401a, 401c, 401d, 466, 868, 1203a, 1699a, 1699b, 1713}

Anhydrous chlorine in butane reacts with a dixanthogen to form a sulfene chloride: ⁴⁵⁷



With a disulfide a redistribution takes place: ⁹³⁷

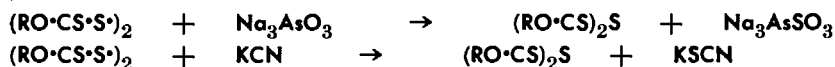


Sodium sulfide serves as a catalyst.

The lower dixanthogens are oils, insoluble in water but very soluble in organic solvents.^{213b, 241, 1327c, 1393} They are only moderately stable to heat. The two lower ones give $\text{MeO}\cdot\text{CS}\cdot\text{SMe}$ and $\text{EtO}\cdot\text{CS}\cdot\text{SEt}$. The benzyl compound decomposes into benzyl disulfide, $(\text{PhCH}_2\text{S}\cdot)_2$, when heated at 0.1 mm, and into stilbene at 11 mm. or above.^{213b}

Menthyl dixanthogen, $(\text{C}_{10}\text{H}_{19}\text{OCS}\cdot\text{S})_2$, melts at 93° , $[\text{M}]_D -1069.9$, and the corresponding thioanhydride, $(\text{C}_{10}\text{H}_{19}\text{OCS})_2\text{S}$ at 149° .^{297a, 298b, 298c, 1575} The influence of temperature on the anomalous rotatory dispersion has been studied.³⁰² The menthyl dixanthogen, $\text{C}_{10}\text{H}_{19}\text{O}\cdot\text{CS}\cdot\text{S}_2\cdot\text{CS}\cdot\text{OC}_{10}\text{H}_{19}$, is rhombic.¹³

A dixanthogen gives up sulfur to sodium arsenite ⁶⁹² or potassium cyanide: ^{390, 1721c, 1722}



The xanthogen monosulfides or xanthic thioanhydrides are either low melting solids or oils. They can be distilled at 0.5 mm. but not at 20 mm. $(\text{MeO}\cdot\text{CS})_2\text{S}$,^{1721c, 1722} $(\text{EtO}\cdot\text{CS})_2\text{S}$, $(\text{PrO}\cdot\text{CS})_2\text{S}$, $(\text{i-BuO}\cdot\text{CS})_2\text{S}$,¹⁷²² $(\text{HexO}\cdot\text{CS})_2\text{S}$,^{241, 1721c} $(\text{EtOCH}_2\text{CH}_2\text{O}\cdot\text{CS})_2\text{S}$, and $(\text{PhCH}_2\text{O}\cdot\text{CS})_2\text{S}$ ²⁴¹ have been prepared.

Dixanthogen, $(\text{EtO}\cdot\text{CS}\cdot\text{S}\cdot)_2$, is effective against body lice ^{219, 649, 919, 1536} and repels ticks.¹⁵²⁵ It is about as toxic as dodecyl thiocyanate.²¹⁹ In an ointment on gauze it prevents fly oviposition on meat.¹⁷⁹⁴ Aqueous emulsions for use in veterinary practice can be prepared using sulfurated and naphthenic oils in place of soap.⁹²¹ Dixanthogens have been tried in treatment of skin disease.⁵²⁹ Dixanthogen is said to be useful for weed control.¹³²⁸ Dixanthogen destroys microorganisms, lowers blood pressure and increases rate of respiration of a rabbit.⁸¹¹

Dixanthogens are useful in flotation.^{679, 680} The xanthate and chloride of lime may be added to the mineral pulp.¹⁷⁶⁴ Dixanthogens from secondary alcohols are claimed.¹⁰⁶⁴ Dixanthogen is a powerful collector for coals of all ranks except lignites.⁸⁰³ Di-i-propylxanthogen disulfide is useful as a regulating agent in butadiene polymerization.⁵²⁰ Dixanthogens in which the alkyls

contain at least three carbon atoms are said to increase the film strength of lubricating oils.^{1648b} The butyl compound^{3, 1211} and others²⁷⁹ are claimed as vulcanization accelerators. They influence favorably the polymerization of butadiene hydrocarbons or of chloroprene.^{818b} Dixanthogen gave extra resistance to ultraviolet light to a vulcanized GR-S mixture.⁸⁵ The *i*-propyl compound serves as a modifier in polymerization¹²⁹⁰ and for stabilization of polysulfone resins.³⁶⁵ A mixture of a xanthogen and a mercaptan modifier is said to be useful in the polymerization of 1,3-butadiene hydrocarbons.⁵⁹² Free-radical-initiated emulsion polymerization reactions are stopped by a solution of a dixanthogen polysulfide in inorganic polysulfides.³⁴

Industrial Applications of Xanthates

Flotation

Xanthates are important in the recovery of minerals by flotation. This subject is large and can be only sketched here. According to a review by Petersen,^{1281b} the basic patent on flotation, issued in 1905,^{1158a} was followed by over 2000 others in the next 20 years. German patents were reviewed by Friedmann in 1921.⁵⁸⁴ The use of xanthates in flotation has been reviewed by Howat.⁸⁰⁷

The fundamentals of flotation have been considered.^{1494, 1680a} Surface tension is important.^{436, 438} Various xanthates have been prepared and compared as to activity.^{53, 437, 1488a, 1579, 1656} Purified xanthates give better results.^{1488a}

The adsorption of xanthates on various minerals has been investigated.^{543, 615, 1360, 1492, 1497, 1577b, 1680b, 1717a, 1717b} The anion has an influence¹⁶⁸¹ and the wetting power of the solutions is to be considered.^{421, 1335, 1336} Reactions of the xanthates with galena have been studied.^{109, 616, 617, 714, 946, 1596, 1667, 1733} Dixanthogen is taken up by galena from a water suspension.⁶¹⁷ The influence of adsorbed films on potential differences between solids and aqueous solutions of xanthates has been studied.¹⁰³²

There has been considerable interest in xanthates prepared from higher alcohols, particularly *n*-butyl. The xanthates from *i*-butyl and *n*-butyl alcohols are highly effective,^{53, 1335, 1488a, 1579, 1656} so is the one from *i*-amyl.^{53, 1488a, 1561} Those from glycols are less active.⁹⁰³ Those from *s*-butyl,^{293, 1237b, 1387, 1388c} *t*-butyl^{1385, 1388b} and *i*-propyl¹³⁸⁵ and been claimed. The ones made

from the higher alcohols are more effective.¹⁴⁹² Those derived from the alcohols obtained by the oxidation of kerosene or other oils are said to be suitable for flotation,⁸⁴⁸ as are those from the hexahydrocresoles.^{374, 1116} Xanthates from abietyl and hydroabietyl alcohols are recommended as collectors and wetting agents.¹³³⁴ Those from saturated and unsaturated alcohols of six to eighteen carbon atoms are claimed as flotation and wetting agents and vulcanization accelerators.⁶⁵⁹ Some from lower unsaturated alcohols are recommended as flotation agents, also as insecticides and vulcanization accelerators.^{671, 672}

Soluble xanthates are used in differential flotation.¹⁶⁸⁴ They are usually employed in admixture with the other agents such as pine oil, cresylic acids, and mineral oils.^{902a, 1010, 1011, 1055, 1117, 1158b, 1512} The heavy residual oil from the rectification of fusel oil gives good results with potassium ethyl xanthate.¹⁴ A complex salt such as a ferricyanide may be added also.^{1158c} A protective colloid, such as starch, may be added to the mixture of agents.^{1159, 1511, 1739} Flotation may be effected by a xanthate and sodium silicate.¹⁰¹⁰ An alkali xanthate is used with an alkali chloride.¹¹⁸⁵ Potassium ethyl xanthate aids in cleaning fine coal.^{1281a}

Xanthates as Pesticides

The effectiveness of xanthates against plant lice^{1803b} and in the soil against the root knot nematode¹²⁵⁰ has been attributed to carbon disulfide liberated in their slow decomposition. Potassium ethyl xanthate is fairly toxic to this pest.^{634a} Potassium *i*-amyl xanthate has been recommended for use against *phylloxera*.^{1803a}

Potassium ethyl xanthate is lethal to the larvae of a potato pest.⁸¹³ Sodium amyl xanthate may be used with Paris green.¹¹⁹⁷ Xanthates from *i*-propyl, *t*-butyl,¹³⁸⁵ and *s*-butyl^{1237b, 1387, 1388c} alcohols are insecticides. Those from primary alcohols containing six to fifteen carbon atoms are effective insecticides, particularly the one from lauryl alcohol.⁶⁵⁹ Remarkable results are claimed from those made from the hydroxyl compounds obtained by the catalytic oxidation of petroleum hydrocarbons.⁸⁴⁸ The ethyl and butyl xanthates are the best but even these are not highly effective fungicides.⁶³⁹ Potassium ethyl xanthate mixed with soil kills Japanese beetle larvae.⁵⁴⁹ Cadmium xanthate is claimed as a seed disinfectant.¹¹⁴⁵ Methyl potassium xanthate is 98% effec-

tive against coddling moth larvae.¹⁰⁶⁷ Soils retain a significant amount of the sulfur of potassium xanthate.³²⁶

Sodium ethyl xanthate is toxic to the aerial parts of herbacious plants.⁷³⁴ Sodium *i*-propyl xanthate is an herbicide.^{80, 527, 1328} Xanthates stimulate growth of some plants.⁸⁴⁰ Potassium butyl xanthate has given good results in stimulating root formation in plants.¹⁶³⁰ Potassium ethyl xanthate poisoned "enzyme preparations" in oxidation of ascorbic acid¹⁵⁶⁷ and of N-acetylindoxyl,⁹² and it inhibited photosynthesis in *chlorella* cells.⁶⁶⁰ The conversion of ammonium ions to nitrite and nitrate in soil is inhibited by ethyl potassium xanthate, a copper-enzyme poison.^{202, 347, 433, 839, 883, 884, 980, 995, 1582}

Other Applications of Xanthates

The phenomena of vulcanization have been studied with the aid of potassium xanthate.¹⁴⁷² A number of xanthic salts have been compared as vulcanization accelerators. The zinc *i*-propyl gave the best results.^{1643a} In a later study the butyl compound was found to be the most efficient.⁹³⁰ Patent claims have been made for metal alkyl xanthates in general,^{225c, 266} for those from *i*-propyl^{394, 1385} and *t*-butyl alcohols¹³⁸⁵ and for zinc *i*-propyl,^{1410, 1642} butyl,¹⁴⁹¹ *i*-butyl,¹⁴¹⁰ and other alkyl xanthates.^{204, 659} Xanthates have been used with dithiocarbamates.^{266, 554, 1491}

The ethyl compound is of interest in photography as a desensitizer.¹⁵⁴ Alkali xanthates from alcohols above octyl may be used as textile assistants. The alcohols from their decomposition may remain in the fiber as softening or delustering agents.^{432b} The xanthic acids from high molecular weight alcohols may be incorporated in cosmetics.⁷⁴⁹ Some potassium xanthates are promoters for the dropwise condensation of steam.¹²⁷ Ammonium, substituted ammonium, or alkali metal xanthates have been patented for the formation of plastics from 2-chlor-1,3-butadiene polymers.^{484a}

Metal xanthates are proposed for use as drying substances.⁹⁷⁰

Certain xanthates have been recommended as additions to lubricating oils to reduce oxidation and corrosion.^{1026, 1072} A metal salt such as nickel amyl xanthate,¹⁶⁸⁶ potassium tridecyl xanthate,²⁴ or zinc *i*-propyl xanthate¹⁰⁷⁷ may be added to a lubricating oil.

The gold salts of propyl, *i*-propyl, butyl, and *i*-butyl xanthates

are not toxic to non-protein nitrogen in the blood.^{423a} Potassium xanthate is toxic to bull, rabbit, and human sperm.¹⁷²⁵

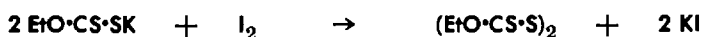
Xanthates in Analysis

The formation of cuprous xanthate was used to detect carbon disulfide in liquids and in coal gas by Vogel. The liquid was mixed with an alcoholic solution of potassium hydroxide, or the gas bubbled through such a solution. Cupric acetate was added to precipitate cuprous xanthate, insoluble in ammonia, which was added to dissolve copper hydroxide.¹⁶⁶⁵ A precipitate was obtained with one cubic foot of gas.^{779a} Carbon disulfide can be determined gravimetrically with alkyl or aryl copper xanthates. Of the xanthates studied for this purpose, the octyl was the most stable to heat.³⁷⁵ The xanthate may be oxidised by permanganate and the sulfate ion precipitated as barium sulfate.¹⁴⁵¹ The precipitated copper compound may be filtered off and washed on the filter with ammonium hydroxide.¹⁵²² The cuprous xanthate may be collected, washed, and weighed.^{1327a} The copper xanthate formed from a gas sample can be compared colorimetrically with that from a known amount of a standard xanthate solution.⁴³⁰ The alcoholic potash in which the carbon disulfide has been taken up is made faintly acid with acetic acid. Standard copper acetate solution is added and the excess cupric ion titrated with iodine.^{721, 810, 1359, 1401} The precipitated cuprous xanthate may be dissolved and the copper determined iodometrically²²⁸ or electrolytically.⁷¹³

Carbon disulfide may be taken up in alcoholic potash, cream of tartar added, and the xanthate titrated with a standard solution of copper sulfate containing Rochelle salt. Conversely, caustic alkalies, mixed with carbonate and other salts which do not react with carbon disulfide, may be converted to xanthates and titrated.⁶⁶⁸ The use of carbon disulfide against *phylloxera* made it necessary to determine it in the soil which is done by converting it to the xanthate. The solution is made slightly acid with acetic acid and titrated with standard copper sulfate with potassium ferrocyanide as indicator.^{1065, 1066} This method has been used by many.^{111, 867, 1547} Very small amounts of carbon disulfide may be determined by the xanthate method, down to 0.005 mg.¹⁰⁶¹ As little as 0.0005 mg. in 10 cc. of blood can be estimated.⁷³³ The xanthate may be transformed into an ester¹¹³⁴ or precipitated as a lead salt.^{247, 1154, 1407} Carbon disulfide in

ethereal oils can be determined by adding absolute alcohol and distilling up to 82°. Potassium hydroxide and ammonium molybdate are added to the distillate which is made slightly acid. A red-violet color develops.^{1098b}

Carbon disulfide has been identified in mustard oil,^{781c, 1057} in benzene,^{1225, 1661} in other oils,¹⁶⁵⁴ in air,⁶¹³ and in carbon tetrachloride¹³²⁶ by the copper xanthate test and estimated by titrating the xanthate with iodine^{124, 228, 342, 613, 779a, 1326} or bromine:



The iodometric titration of a xanthate is the most convenient method of determining carbon disulfide.^{1128b}

Advantage may be taken of the fact that free xanthic acid is readily decomposed:



An excess of standard acid is added to a neutral solution containing a xanthate. After a few minutes the solution is back titrated with barium hydroxide.^{769, 788b} Or the xanthate and impurities may be titrated with iodine in one aliquot while in another the xanthic acid is destroyed by acidification and the impurities titrated.^{1488b}

The heavy metal xanthates have distinctive colors and differ considerably in solubility in water, in dilute ammonium hydroxide, and in acids.¹²⁸⁴ These characteristics may be used in qualitative analysis. Copper and nickel may be separated; in dilute slightly ammoniacal solution copper xanthate is precipitated while nickel remains in solution as a complex salt.^{1701a} A system of analysis for the heavy metals by means of xanthate has been worked out.^{277, 1702} Xanthates may be used for chromatographic analysis for molybdenum, copper, nickel, and cobalt.⁴²

Studies have been made of the volumetric determination of copper by xanthate.^{1242, 1401} Qualitatively, copper can be detected down to one part in 900,000 of water.¹⁶⁶⁹ However, the xanthate test for copper is only about one-hundredth as sensitive as the diethyldithiocarbamate.²²⁹ The colorimetric determinations^{1705, 1740} by the two reagents have been contrasted.³¹³ The xanthate tests for copper and cobalt have been compared with other tests.¹⁶²⁹ In the analysis of minerals, copper and cobalt may be precipitated as xanthates.⁶ The chromatographic reso-

lution of cobalt complexes with certain xanthates has been studied.⁹⁶⁰ The solubility of cobalt xanthates in organic solvents has been used for its detection, determination, and separation from other metals.⁹⁶⁹

Fermate, $(\text{Me}_2\text{N}\cdot\text{CS}\cdot\text{S})_3\text{Fe}$, which is used as a fungicide, can be determined by decomposing it with dilute citric acid and the liberated carbon disulfide carried into an ammoniacal solution of cupric acetate which is extracted with chloroform and the yellow xanthate determined colorimetrically.⁴⁴²

Xanthates are of service for the determination of nickel and cobalt.^{243, 245b, 260, 323a, 534} For the separation of the two metals advantage may be taken of the fact that the nickel salt is soluble in ammonium hydroxide and the cobalt is not^{323a, 1284} or that the nickel methyl xanthate, $(\text{MeO}\cdot\text{CS}\cdot\text{S})_2\text{Ni}$, is soluble.⁵³⁴

Xanthates have been employed in detecting and determining molybdenum.^{512, 673, 711, 955, 997, 1051, 1098a, 1263, 1292, 1513a, 1590b, 1602} This may be done colorimetrically.^{997, 1098a} Spot tests are recommended for steel analysis.^{512, 1602} The sensitivity increases with the molecular weight of the alcohol used for making the xanthate up to cetyl.^{1590b} This has been doubted.^{1098a} The limit has been given as 0.0005 mg. per cc. or 1 in 2,000,000.^{1590b}

Xanthate may be used for the estimation of zinc and cadmium.¹⁰³ A micro separation of zinc and aluminum may be effected by xanthate.¹⁷⁰⁰ Tellurium can be detected.^{518.5} Arsenic can be separated and identified as the xanthate, $(\text{EtO}\cdot\text{CS}\cdot\text{S})_3\text{As}$,^{1381, 1593 m. 95°.}¹⁵⁹³ Arsenite can be separated quantitatively from arsenate.³⁵³ Traces of lead may be determined by production of air avidity in surface of sphalerite in sodium xanthate solution.^{1577a}

Viscose, cellulose xanthate, gives characteristic colors with heavy metal ions.^{1590a}

Commercial xanthates may be analyzed argentometrically.¹¹⁴³ An excess of standard silver nitrate is added and back titrated with potassium thiocyanate.¹⁰⁹¹ They may be precipitated and weighed as lead xanthate,¹⁰⁹⁰ or determined potentiometrically.¹²⁴⁵ Directions for analysis of technical xanthates have been given.⁹⁴¹ Water in xanthates may be determined.¹⁰²⁴

Alkali xanthates can be identified by converting them to the palladium salts which differ somewhat in color and have distinctive melting points.^{213d}

The sulfur in xanthates may be determined by oxidation to the sulfate by permanganate⁶¹⁴ or hypochlorous acid.¹³⁹⁰ The $-\text{CS}-$ group in thion- or trithiocarbonates may be determined by a solution of sodium azide and iodine.⁵²⁸

Azidodithiocarbonic Acid

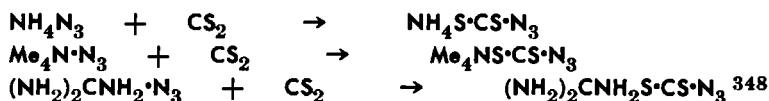
This does not really belong in this section but in its formation and in its reactions it so closely follows the xanthic acids that it is convenient to consider it here.

If 7.5 g. of carbon disulfide is added to 6 g. sodium azide in 25 cc. of water at 40–50° combination takes place. The solution is filtered and concentrated by standing over phosphoric anhydride. On cooling the concentrated solution, the sodium salt $\text{N}_3\text{CS}\cdot\text{SNa}\cdot 4\text{H}_2\text{O}$ crystallizes out.



This salt is stable in a closed container below 10°. The anhydrous salt explodes by shock or by heat.¹⁵⁴⁵ The potassium salt, similarly prepared, is anhydrous. It deliquesces rapidly and dissolves in 0.22 parts of water. The salt and its aqueous solution are stable below 10°. The dry salt is sensitive to shock. It is soluble in methanol and acetone but insoluble in most other organic solvents.^{196b} The absorption of carbon disulfide vapor, even when mixed with other gases, by an aqueous solution of sodium azide is quantitative.³⁷⁷

The ammonium, tetramethylammonium,⁵¹ and guanidine salts are prepared similarly:



The sodium salt crystallizes with either four or two molecules of water, the lithium with only one. The potassium, rubidium, and cesium salts are anhydrous.¹⁹⁴ The heavy metal salts are precipitated when solutions containing the proper ions are mixed. They are fearfully explosive when dry.^{1529, 1545}

The cesium and rubidium salts are photosensitive. On exposure to daylight they assume, respectively, light red and violet red tints which gradually fade out in the dark.^{194, 348}

Azidodithiocarbonic acid, $\text{HS}\cdot\text{CS}\cdot\text{N}_3$, is formed by the direct

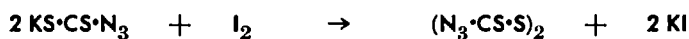
union of hydrazoic acid and carbon disulfide in ether solution.¹²⁴⁹ When an aqueous solution of hydrazoic acid is shaken with carbon disulfide and silver nitrate added, silver azidodithiocarbonate is precipitated. The usual method of preparing the acid is to add cold concentrated hydrochloric acid to a cold concentrated solution of the sodium salt. The white crystalline precipitate is washed with ice water and dried on a porous plate. It is stable in the dark below 10°. ¹⁵³⁰ The preparation is fully described by Smith.¹⁵²⁷

It is a moderately strong acid, $K = 2.14 \times 10^{-2}$ at 25°. ^{718, 1528} The equivalent conductivity of the ion $N_3 \cdot CS \cdot S^-$ is 41.7 at 25°. ¹⁵²⁸ It can be titrated with methyl red as indicator and can be determined iodometrically or by the Volhard method with silver nitrate.

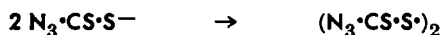
It decomposes into thiocyanic acid, sulfur, and nitrogen. ^{196b, 198, 377, 1530}



Azidocarbon disulfide is formed when iodine reacts with a salt of azidodithiocarbonic acid:



This reaction is slightly reversible; if the azidocarbon disulfide is added to potassium iodide solution containing starch, a blue color develops. The disulfide is formed also by the electrolysis ^{196b, 1530} of the potassium salt:

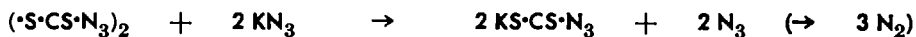


The electrode potential of the azidocarbon disulfide-azidodithiocarbonate electrode has been measured and found to be 0.275 volts. ^{1647.}

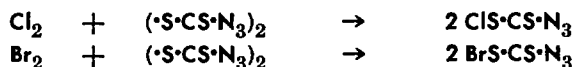
The disulfide is a white crystalline solid slightly soluble in water, moderately soluble in carbon disulfide and benzene, and freely soluble in acetone and ethyl acetate. It is stable at 0° but decomposes at room temperature: ^{195, 197, 1732}



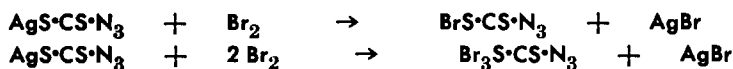
Like dithiocyanogen it is a pseudohalogen and serves as an oxidising agent. It reacts with potassium azide: ^{196a}



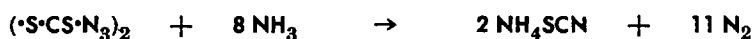
It seems more natural to write $N_3 \cdot N_3$ as the intermediate product. Chlorine and bromine react with it explosively but in certain organic solvents addition takes place:



The chlorine compound is a pungent yellow oil, the bromine a white amorphous powder, evidently polymeric. Bromine reacts with silver azidodithiocarbonate in two ways: ⁶⁰⁹



With ammonia there is elimination of nitrogen: ¹⁷³²



Xanthic Esters, RO·CS·SR

Preparation

Esters of this type are the best known and most important of the thiocarbonates. Many have been made, some for their own sakes and others as intermediates. They are prepared by alkylating xanthic salts and for that reason are called xanthic esters, or alkyl xanthates. Thus $EtO \cdot CS \cdot SPr$ is propyl xanthate, or specifically propyl ethylxanthate. Xanthic acid is $EtO \cdot CS \cdot SH$ and its salts and esters are $EtO \cdot CS \cdot SK$ and $EtO \cdot CS \cdot SR$. When we use the terms alcohol, mercaptan, and xanthate we mean the ethyl compounds $EtOH$, $EtSH$, and $EtO \cdot CS \cdot SK$ since they were the first compounds of their classes to become known. When other alkyls are involved they must be designated. Thus $PrOH$, $PrSH$, and $PrO \cdot CS \cdot SK$ are propyl alcohol, propyl mercaptan, and potassium propylxanthate.

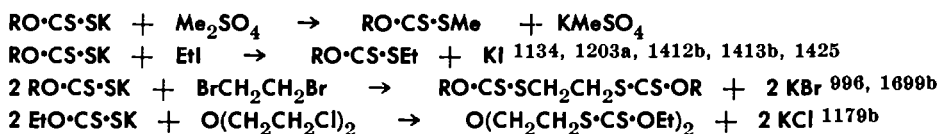
Potassium xanthate, as has been shown in a preceding section, is one of the easiest compounds to prepare.



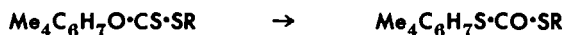
As the potassium is joined to a bivalent sulfur atom alkylation takes place easily and completely: ^{401c}



Since it has become available the more active dimethyl sulfate is preferred: ⁴⁸⁶



The reaction of alkali xanthate with an ethylene halide is irregular and may yield carbon oxysulfide, hydrogen sulfide, and olefin. The percent of the olefin increases with branching in the ethylene halide.⁶¹⁸ Cyclohexyl iodide reacts with potassium xanthate.¹⁵³ 2,2,6,6-Tetramethylcyclohexanol has been xanthated and made to react with alkyl halides. When these esters are heated to 300° they isomerize: ^{974a}



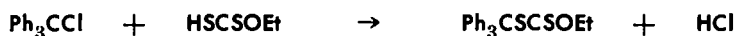
The properties of these esters are in the lists of physical properties. Methyl fenchyl xanthate, $[\alpha]_{24/D} -138.28^\circ$, isomerizes similarly; the product, $b_{10} 173^\circ$, $[\alpha]_{24/D} -24.64^\circ$, gives thiofenchol, $[\alpha] -24.64^\circ$ on hydrolysis.⁹⁷³

A number of esters, $\text{PhC}(:\text{NPh})\text{S}\cdot\text{CS}\cdot\text{OR}$, have been prepared.^{295c} The methyl and ethyl esters have been prepared from xanthated borneol and their rotations, absorption curves,^{301a} and crystal forms studied.^{40, 1294} Methyl esters of α - and β -norborneol have also been prepared.¹⁶²²

Methyl magnesium⁵⁸⁹ and allyl potassium¹²⁴³ xanthates react well with ethyl bromide. Even methyl nitrate can be used as the alkylating agent.^{410a}

It is not necessary to isolate the metal xanthate.^{1106, 1727} Powdered sodium hydroxide may be added to the alcohol in carbon disulfide and methyl iodide added.¹⁶⁶² Or carbon disulfide is added to a methanol solution of potassium hydroxide. As soon as it is dissolved dimethyl sulfate is put in.⁷⁵³ Even in cases in which it is impossible to isolate the metal xanthate, the ester may be obtained by adding methyl iodide to the mixture of carbon disulfide and sodium alcoholate.¹⁶²⁰

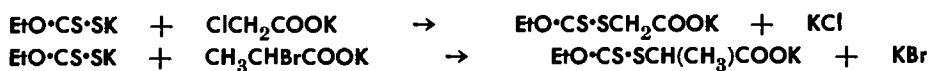
The free xanthic acid reacts with trityl chloride: ¹¹⁶



Xanthic esters can be obtained from the ester chlorides, $\text{RO}\cdot\text{CSCL}$: ^{1365a}



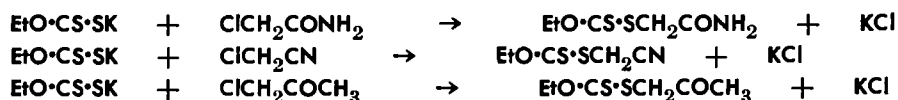
Chloracetic and other α -halogen aliphatic acids react regularly with a xanthate: 114b, 114c, 572a, 786a, 790c, 1634



Esters of chloracetic acid react well: 264, 1634



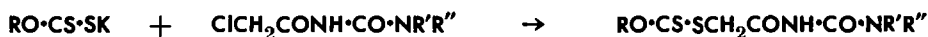
Other derivatives of chloracetic acid and most compounds containing active halogens react readily: 522, 1366, 1634



Many of the compounds obtained by reacting chloracetanilide with xanthates are solids and are useful for identification: 792

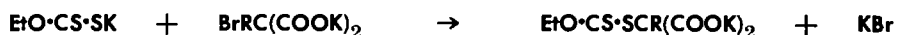


Since the xanthates are so readily made from alcohols, this offers a convenient way of identifying alcohols. DL-Borneol and menthol were treated with sodium and then with carbon disulfide which was followed by chloracetamide. The product, $\text{RO}\cdot\text{CS}\cdot\text{SCH}_2\text{CONH}_2$, from borneol melted at 88° and that from menthol at 98.9° , $[\alpha]_D -64.5^\circ$.⁷⁹³ Various metal xanthates react with chloracetyl carbamides:

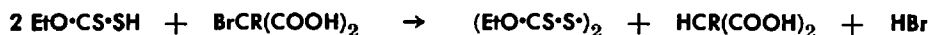


R may be methyl, ethyl, etc., and R' and R'' aryl or alkyl groups.⁵⁷⁸

The kinetics of the reaction of chlor- or brom-acetic acid with xanthate ions has been extensively studied.^{931, 1692} The reaction is of the second order.^{787d} The rates of the reaction of alkylbromomalonic acids have been compared:



The relative rates when R is H, *i*-Pr, Et, or Ph are: 9.8, 3.6, 1.1 and 1. It is remarkable that the hindrance by the *i*-propyl group is less than that of the ethyl. In acid solution the reaction is:¹¹⁷



The stereo-isomeric xanthosuccinic acids have been prepared from the bromo-derivatives: ^{787c}, ^{788d}, ^{789a}, ⁷⁹¹

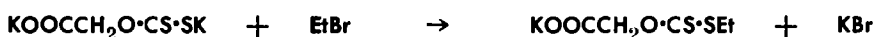


A trichlorobenzyl alkyl xanthate ester, $\text{Cl}_3\text{C}_6\text{H}_2\text{CH}_2\text{S} \cdot \text{CS} \cdot \text{OR}$, from trichlorobenzyl chloride and a xanthate,¹³¹ and dixanthates, from alkylxanthates and dihalides,⁹⁹⁶ are said to be useful in a high pressure lubricant.¹³¹ The esters, $p\text{-C}_6\text{H}_4(\text{CH}_2\text{SCSOR})_2$ and $(\text{CH}_2\text{SCSOR})_2$, show insecticidal activity^{1795c} while the esters, $5,3,6\text{-Me}(\text{O}_2\text{N})(\text{HO})\text{C}_6\text{H}_2\text{CH}_2\text{SCSOR}$, have valuable fungicide properties.⁵²¹ Some diesters having a long carbon chain, $\text{RO} \cdot \text{CS} \cdot \text{S}(\text{CH}_2)_x\text{S} \cdot \text{CSOR}'$, promote perfect dropwise condensation of steam on a cooled metal surface.¹²⁷ Potassium ethyl xanthate and methyl dichlorostearate give a monochloro xanthic ester which is said to be useful as a corrosion inhibitor and a film-strength improver in lubricating oils.¹⁰²⁵

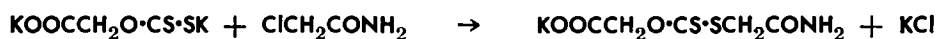
Glycolic acid reacts with carbon disulfide and alkali:



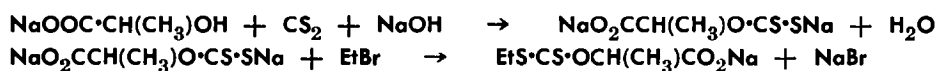
This can be ethylated:



The acid from this is isomeric with $\text{EtO} \cdot \text{CS} \cdot \text{SCH}_2\text{COOH}$ from xanthate and chloracetic acid.^{786a}, ^{786c} Chloracetamide reacts well: ⁵



This amide melts at 130° . Some of the amide $\text{SC}(\text{SCH}_2\text{CONH}_2)_2$ is obtained as a byproduct. Lactic acid may be put through similar reactions:



The DL-acid from this melts at $73\text{--}4^\circ$ and is soluble in water to the extent of 3.67 g./l. It has been resolved. The D(−) acid melts at $36\text{--}7^\circ$, $[\alpha]_D -9.7^\circ$, solubility in water 6.37 g./l.^{790b} Malic acid has been studied.^{790a} The isomeric acids:



have been contrasted; $[\alpha]_{25/D}$ is 104.1° for I and 36.6° for II.^{570b} α -Xanthobutyric⁵⁷³ and α -xanthopropionic^{572b} acids have been

resolved. A comparison has been made between the optically active dithiocarbethoxy derivatives of malic and aspartic acids: ^{571a}



Acetobromoglucose has been made to react with potassium xanthate.¹⁴⁵⁵ Similarly triacetylxylose ethylxanthate has been made from acetobromoxylose.⁶¹⁹ Conversely α -methylglucoside,¹⁰²⁰ and many similar compounds,^{562, 1758} have been converted to xanthate salts by treatment with barium hydroxide and carbon disulfide and then methylated. Methyl α -methylglucoside xanthate has rotation $[\alpha]_{\text{D}}^{20} 122.7^\circ$, the β -isomer has $[\alpha]_{\text{D}}^{20} -5.01^\circ$.¹⁰²⁰

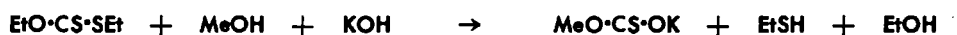
Thiophosgene reacts with *o*-hydroxythiophenol to form a cyclic xanthate ester, m. 98° .⁶⁶²

Hydrolysis of Xanthic Esters

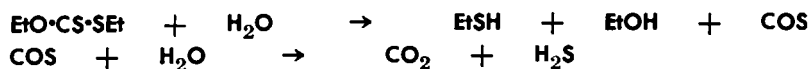
These esters are easily hydrolyzed.⁸⁷⁵ A mercaptan ester is more readily hydrolyzed than one from an alcohol,¹³³⁸ and it has been claimed that hydrolysis may be stopped at the half ester, the mercaptan being eliminated: ^{1412b, 1413b, 1450}



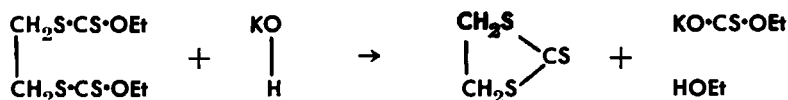
Alcoholysis may intervene:



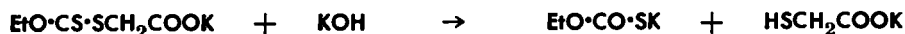
Complete hydrolysis eventuates in mercaptan, alcohol, carbon dioxide, and hydrogen sulfide: ¹⁴⁵⁰



There must be disproportionation since potassium dithiocarbonate has never been reported: ⁵⁶⁸



Carboxymethyl xanthate, $\text{EtO}\cdot\text{CS}\cdot\text{SCH}_2\text{COOH}$, is said to be hydrolyzed partially:



When it is heated in neutral solution some of the trithiocarbonate, $\text{SC}(\text{SCH}_2\text{COOH})_2$, is formed.^{114b, 786a, 786c} Its saponification gives some of the same as a by-product.^{114c} The ethylene ester loses carbon oxysulfide when it is heated with ammonia:^{814c}

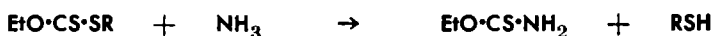


The ethylene dithiocarbonate has been obtained as a by-product in the saponification of a complex xanthate ester.¹⁸⁰⁰

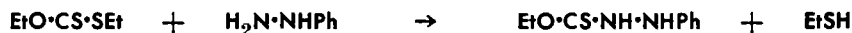
Ammonolysis of Xanthic Esters

As this is an important method of preparing thiourethanes it is considered more fully in that section.

Ammonolysis follows the same course as hydrolysis. The mercaptan is displaced in preference to the alcohol: ^{271a, 297a, 327, 417, 786a, 786c, 786d, 787b, 790c, 1243, 1412b, 1413b, 1450}



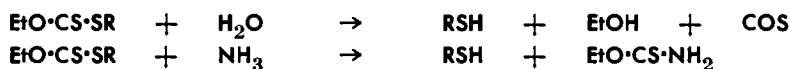
Ammonia (10%) on isofenchylxanthic ester gives two isomeric amides, $\text{C}_{10}\text{H}_{17}\text{O}\cdot\text{CS}\cdot\text{NH}_2$, one an oil, the other a solid melting at 70° , $[\alpha]_D -37.77^\circ$.^{1206b} Menthyl, bornyl, fenchyl, and other terpene xanthic esters behave somewhat similarly.^{297b, 297d, 298a} The selective degradation of a peptide may be brought about by the action of a dialkyl xanthate. The terminal amino acid is removed and may be identified by the melting point of the resultant N-Thionocarbalkoxy derivative.⁹⁰⁷ A hydrazine reacts as an amine:^{213a}



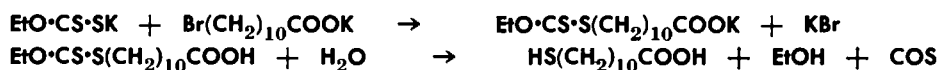
Mercaptans from Xanthate Esters

This has already been considered in the mercaptan chapter, Vol. I, page 30, as a preparation method.

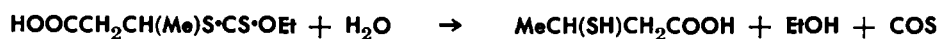
Since potassium xanthate is so readily prepared and since it reacts so easily and completely with alkyl halides, sulfates, and the like, the hydrolysis or ammonolysis of xanthic esters is a convenient way of preparing mercaptans:



The over-all yield from the alkyl halide is high. A special advantage is that there is no opportunity for the formation of the alkyl sulfide, RSR. Thus 10-bromoundecylic acid has been converted to the corresponding mercaptoacid: ^{78, 317}



β -Mercaptobutyric acid has been obtained by the hydrolysis of a xanthate ester: ⁸⁶⁶

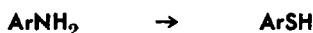


Racemic α -xanthopropionic acid was resolved and the active mercaptopropionic acids obtained by ammonolysis. ^{572b}

The method has been useful for making aromatic mercaptans from diazonium halides:

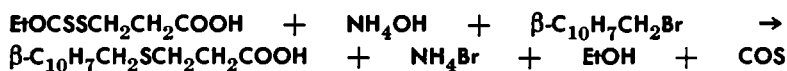


This has the effect of converting an aromatic amine to the corresponding mercaptan: ^{1001, 1002, 1062, 1243}



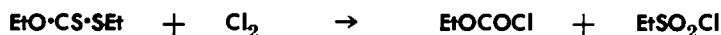
The reaction does not always go so simply; $\text{ArS}\cdot\text{CO}\cdot\text{SAr}$ may be formed also. ⁷⁷⁷

A sulfide may be made without isolating the mercaptan by adding a halide to the reaction mixture: ^{571a}



Other Reactions of Xanthic Esters

Chlorination of a xanthate gives a sulfonyl chloride and a chloroformic ester: ⁴⁵⁶

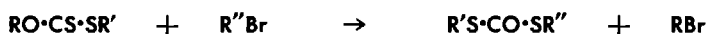


If anhydrous chlorine is used in liquid butane a sulfenyl chloride is formed: ⁴⁵⁷

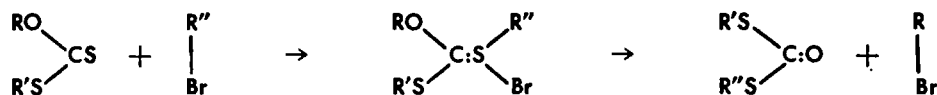


A sulfenyl chloride, $c\text{-HexS}\cdot\text{CCl}_2\cdot\text{SCl}$, results when a mixture of cyclohexane and carbon disulfide is chlorinated under the influence of light. ⁹²⁰

Xanthic esters undergo an interesting reaction with alkyl halides:



A sulfonium compound is probably the intermediate:



Xanthogenacetic acid and bromoacetic acid heated at 120° for three hours give the acid, $\text{OC}(\text{SCH}_2\text{COOH})_2$. Similarly $\text{OC}(\text{SCH}_2\text{CH}_2\text{COOH})_2$, is obtained from β -xanthogenpropionic acid and β -bromopropionic acid.^{114d} Another example is:



The reduction with lithium aluminum hydride of the carbonyl and xanthate functions of certain xanthic esters, produces substituted mercapto ethanols.⁴⁵² Hydrogenation with a sulfactive catalyst gives methyl mercaptan.⁹⁸⁹

Pyrolysis of Xanthic Esters

This has been a much used method of preparing unsaturated hydrocarbons from alcohols, particularly in the terpene group:



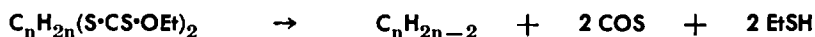
The second alkyl is preferably methyl since methyl mercaptan cannot lose hydrogen sulfide. Ethyl alcohol loses water more readily than ethyl mercaptan parts with hydrogen sulfide. Ethyl xanthate should give the mercaptan:



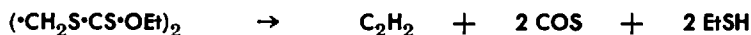
Apparently this has not been demonstrated. In *t*-butyl xanthate, *t*-BuS·CS·OEt, things would be more evenly balanced. Dihydrocarveol, menthol, thujol, borneol, 4-methylborneol, 4-methylisoborneol, fenchol, and cholesterol have been converted to unsaturated hydrocarbons in this way.^{295b, 295c, 296, 297a, 297b, 297c, 299, 300, 1487}

The kinetics of the Chugaev reaction with cholesteryl xanthates, the methyl trithiocarbonate of cholesteryl, and other cholesteryl compounds all show first order rate constants. These

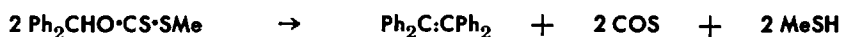
compounds decompose according to a six membered ring transition state.¹²⁴⁰ A mechanism has been proposed for the reaction.¹⁵⁶³ The pyrolysis of certain xanthic esters to form olefins, has been used in the study of cis-trans isomerism.^{16, 349, 809} Bornylene^{182, 953, 1068} 6-methylbornylene,²⁰⁶ 4-methylcyclohexene,^{1106, 1107, 1108} methylenecyclohexene, $C_8H_{10}:CH_2$,¹⁵ fenchene,^{1206a, 1207, 1208, 1323} pericyclocamphene,¹⁸¹ and carene¹¹³⁷ have been prepared by this reaction, so have a number of highly branched aliphatic hydrocarbons.^{556, 557, 1470, 1621, 1727} Xanthic esters from straight chain dibromides decompose so as to give the unsaturated hydrocarbon and a mercaptan: ⁹⁵⁶



Highly branched dienes could not be prepared by this method since the required xanthic esters were not obtained when the dibromides were reacted with ethyl sodium xanthate.^{618, 1585a} Ethylene bromide was caused to react with sodium xanthate and the ester pyrolyzed:



The ester from propylene glycol xanthate gave methylacetylene, carbon disulfide, and ethanol while, $(\cdot CH(CH_3)O\cdot CS\cdot SEt)_2$, from 2,3-butanediol, gave butadiene, carbon oxysulfide, and ethyl mercaptan.¹⁶²⁰ Starting with isobutylene bromide the end product was dimethyl acetylene.¹⁶²¹ The xanthate ester from benzhydrol gives tetraphenylethylene: ⁹⁶⁸



When the methyl benzyl ester, $PhCH_2O\cdot CS\cdot SMe$, is heated rearrangement to the more stable ester $PhCH_2S\cdot CO\cdot SMe$ takes place. At 290° this decomposes, giving 60% stilbene and 25% toluene.^{974a} The methyl xanthate of endo-5-hydroxy-bicyclo-[2,2,1]hept-2-ene decomposed in an atmosphere of nitrogen to form an oil, b. 40–70°.¹²⁶⁴

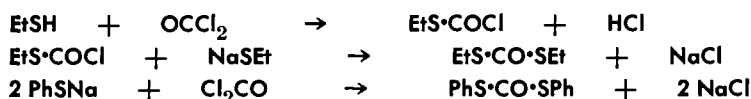
Uses of Xanthic Esters

Methyl ethyl xanthate, $EtO\cdot CS\cdot SMe$, has been found to be moderately effective against codling moth larvae.¹⁰⁶⁷ Various xanthate esters have been recommended as insecticides^{280, 281} and others for protecting wood and seeds against fungi and bac-

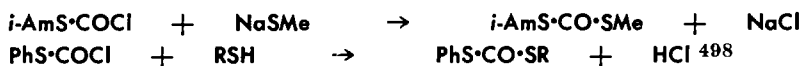
teria.¹⁴⁷ The toxicity and repellancy to the larvae of flies of $\text{EtOCSSCH}_2\text{CMe:CH}_2$ ¹⁰⁴¹ and the invitro antibacterial activity of $p\text{-HOCC}_6\text{H}_4\text{SCSOEt}$ and $o\text{-MeC}_6\text{H}_4\text{SCSOEt}$ ¹³³¹ have been determined. Methyl xanthate exerts a lipotropic effect when administered to male rats on a diet which produces fatty livers.¹³⁶⁹ The diethyl ester, $\text{EtO}\cdot\text{CS}\cdot\text{SEt}$, serves as a rabbit repellent⁵²⁵ and has been claimed as an oxidation inhibitor for turbine oils⁵⁹⁴ and diethyl (xanthyl) ether, $\text{O}(\text{CH}_2\text{CH}_2\text{S}\cdot\text{CS}\cdot\text{OEt})_2$, as a film strength improver for lubricating oils.^{1179a} Allyl esters serve as collectors in froth flotation.^{25b} Certain esters are softening agents in the lacquer^{56, 280, 281} and synthetic resin^{280, 281} industry.

Dithiolcarbonic Esters

The isomeric esters, $\text{RS}\cdot\text{CO}\cdot\text{SR}$, can be obtained by the use of phosgene: ^{213a, 1318, 1412b, 1413a}



A mixed ester can be made: ^{1462b}



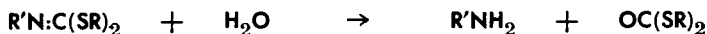
A reaction takes place when phenyl carbonate is rubbed with sodium mercaptide: ¹⁴⁸⁰



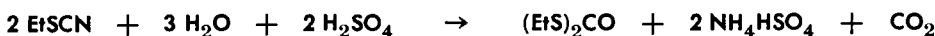
Dithiol esters result from the oxidation of trithiocarbonates: ^{786a, 814c, 1163}



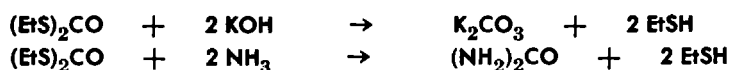
Partial hydrolysis of an iminodithiocarbonate is another method of preparation: ^{408d, 415a, 1688}



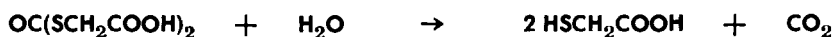
A curious method of formation is by the treatment of an alkyl thiocyanate with sulfuric acid:¹⁴⁵⁰



Alkaline hydrolysis, or treatment with ammonium hydroxide, eliminates the mercaptan: ^{1462b}



The acid, $\text{OC}(\text{SCH}_2\text{COOH})_2$, boiled in neutral aqueous solution is decomposed: ^{786a}



With a limited amount of ammonia or of a primary amine the reaction may stop half way: ^{327, 417}



With a secondary amine it goes no farther than this. ⁴¹⁷

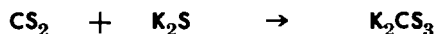
Acetone and carbon disulfide react at room temperature to give a crystalline compound the nature of which is not clear. ^{773a, 1710b}

Dibenzyl dithiocarbonate has been claimed as a vulcanization accelerator. ^{129a} The dithiol ester from thioglycolic acid is a modifier in bulk styrene polymerization. ¹²⁹⁰

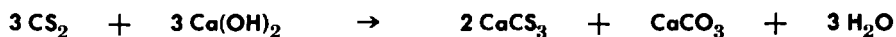
Trithiocarbonic Acid and its Esters

SALTS OF TRITHIOCARBONIC ACID

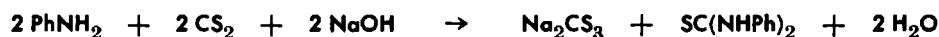
Carbon disulfide dissolves in concentrated aqueous potassium sulfide: ^{786a, 814a, 1660}



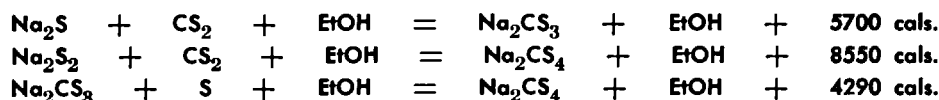
It dissolves also in water containing calcium hydroxide: ¹⁴⁸⁴



Strontium and barium salts are obtained similarly. The sodium salt is obtained by mixing aniline, carbon disulfide, and caustic soda: ^{468a}



In alcohol solution the heat of formation is: ¹⁷⁷⁴



Trithiocarbonates can be made by the addition of carbon disulfide to an ammonium polysulfide solution, ¹¹⁵⁶ to alcoholic ammonia, ^{1007a} or to aqueous ammonium or potassium hydroxide. ^{1710a, 1710b} It has been suggested that the ammonia and carbon disul-

fide of coke oven gas may combine to form ammonium trithiocarbonate and that this decomposes into ammonium thiocyanate and hydrogen sulfide: ^{112, 513, 1161}



Carbon disulfide and aqueous sodium hydroxide give a mixture of carbonate and trithiocarbonate: ¹⁶⁹¹



The kinetics of this reaction has been studied.^{283, 1765} It is probably a two step reaction.²⁸³ This reaction is verified by the fact that the addition of an alkyl halide to the solution gives an alkyl trithiocarbonate.^{1710a, 1710b} In the reaction of carbon disulfide with calcium hydroxide the fact that calcium carbonate is insoluble and precipitates out might be urged as a reason for the disproportionation but both of the sodium salts are soluble.

Double salts, CuNH_4CS_3 and CuKCS_3 , are obtained from cuprous chloride, carbon disulfide, and aqueous ammonium or potassium hydroxides.⁷⁸² Alkylammonium trithiocarbonates, $(\text{NH}_3\text{RS})_2\text{CS}$, have been prepared indirectly.^{1007c} A quaternary ammonium hydroxide such as $\text{PhCH}_2\text{Me}_3\text{NCH}$, combines with carbon disulfide to form a salt which separates as yellow crystals. Heavy metal salts have been made in which half of the quaternary ammonium is replaced by metal. These may be regarded as double salts like the cuprous salt above.³²⁴ The salt, $\text{Fe}_4(\text{NO})_6\text{CS}_3$ has been obtained from ferrous sulfate, sodium nitrite, and sodium trithiocarbonate. The double salt, $\text{Fe}(\text{NO})_2\text{SK}$, reacts with ethyl iodide to give the mercaptide $\text{Fe}(\text{NO})_2\text{SEt}$.¹²⁷⁴

Free trithiocarbonic acid was supposed to have been made by treating sodium amalgam with carbon disulfide, extracting with water, precipitating mercury with hydrogen sulfide, and acidifying with hydrochloric acid, but the product so obtained did not correspond to the pure acid.¹⁰⁴² The pure acid can be prepared by the addition of ammonium¹¹⁵⁶ or calcium trithiocarbonate to cold concentrated hydrochloric acid. It separates as a red oil which is stable in the presence of strong acids and soluble in organic solvents.¹²⁴⁴ It has $d_{17/4}$ 1.47, melts at -30.5° , has surface tension 48.3 dynes/cm. at 12.3° , parachor, 197.3,¹¹⁵⁶ and boils at 50° with decomposition.¹²⁴⁴ Trithiocarbonic acid has $K = 0.001$; when ammonia is added to its ether solution its am-

monium salt is precipitated.⁷¹⁸ It expels carbon dioxide from carbonates. Lead, zinc, and cadmium salts have been prepared. They decompose into metal sulfide and carbon disulfide.¹²⁴⁴ With an aromatic amine the diarylthiourea is obtained from a heavy metal salt: 468a, 469, 1505



The use of salts of dithio- and trithiocarbonic acid in chemical analysis has been suggested.^{470c}

Water-soluble trithiocarbonates are analyzed by decomposing them and determining the liberated carbon disulfide.^{519, 1191} Thiocarbonates may be estimated by conversion into xanthates.⁷⁴³ The detection of sodium trithiocarbonate and sodium perthiocarbonate in the presence of one another and by themselves has been accomplished through ultra violet absorption spectra.¹⁶³²

Sodium trithiocarbonate gives characteristic colored precipitates with heavy metal ions. Analytical procedures have been based on this fact.^{1047, 1056, 1202, 1295} The formation of the salt, Tl_2CS_3 , is a specific test for thallium.¹²⁸⁷ A colorimetric method for nickel is based on the nickel salt NiCS_3 .¹⁰²⁸ Osmium reacts characteristically with sodium trithiocarbonate.^{1513b}

ESTERS OF TRITHIOCARBONIC ACID

Preparation

Ethyl chloride passed into potassium trithiocarbonate gave ethyl trithiocarbonate as a yellow liquid which became red on heating.^{401c, 1473} Ethyl iodide gave the same ester,⁷⁷ so did the bromide.^{1412b}

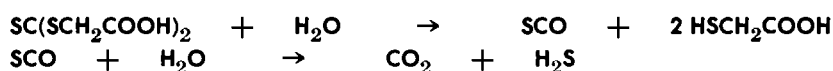
By the action of ethyl iodide and carbon disulfide on sodium amalgam in the presence of moisture Löwig and Scholz obtained a compound $(\text{C}_3\text{H}_5)_2\text{S}_3$ which they regarded as allyl trisulfide.¹⁰⁴³ This experiment has been repeated and the product shown to be ethyl trithiocarbonate, $(\text{C}_2\text{H}_5)_2\text{CS}_3$.¹²¹⁰ Some methyl trithiocarbonate was obtained by methylating the reaction product of sodium amalgam on carbon disulfide.⁵³⁶

Ammonium trithiocarbonate and methyl iodide give a good yield of the methyl ester.^{1710a, 1710b} Methyl calcium sulfate and potassium trithiocarbonate also produced the methyl ester.²²⁷ *i*-Butyl trithiocarbonate was obtained from the iodide.^{1203b} So-

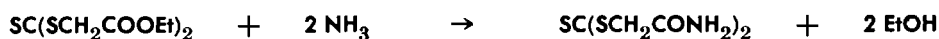
dium trithiocarbonate gave the ethyl ester with ethyl iodide.^{814a}

The methylene ester, CH_2CS_3 , obtained from sodium trithiocarbonate and methylene bromide, was amorphous and probably polymeric.^{814c} The ethylene ester, $(\text{CH}_2)_2\text{CS}_3$, was the product with ethylene bromide.^{814b, 1163} The best method for getting the ethylene trithiocarbonate, in the laboratory, is the reaction of ethylene oxide with an alkali methyl xanthate.^{371, 372} The propylene, *i*-butylene, and *i*-amylene esters were made but not well characterized.^{814c} The trimethylene ester, $\text{CH}_2(\text{CH}_2\text{S})_2\text{CS}$, melts at 80° and the 2-methyltrimethylene, $\text{MeCH}(\text{CH}_2\text{S})_2\text{CS}$, at 74° .¹¹⁵⁷

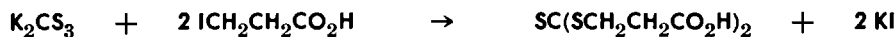
Chloracetic acid gives the thioglycolic acid derivative, $\text{SC}(\text{SCH}_2\text{COOH})_2$,^{114c, 191, 786a} which melts at 173° forming the anhydride.⁵ The methyl and ethyl esters melt at 32° and 47° , respectively. Boiled in alkaline or neutral aqueous solution, this acid is decomposed into thioglycolic acid, carbon dioxide, and hydrogen sulfide. This must be in two steps:



It can be oxidised with permanganate or nitric acid to the dithio, $\text{OC}(\text{SCH}_2\text{COOH})_2$.^{786a} Two isomeric acids, $\text{SC}(\text{SCH}(\text{Me})\text{COOH})_2$, are obtained from α -bromopropionic acid.^{789b} The diamide, $\text{SC}(\text{SCH}_2\text{CONH}_2)_2$, is from chloracetamide. The same amide can be made from the ester and ammonia: ^{786d}



The diethyl amide is made from the reaction of diethylchloracetamide with sodium trithiocarbonate.¹⁴⁷¹ The next higher homolog is from the reaction of β -iodopropionic acid and potassium trithiocarbonate:

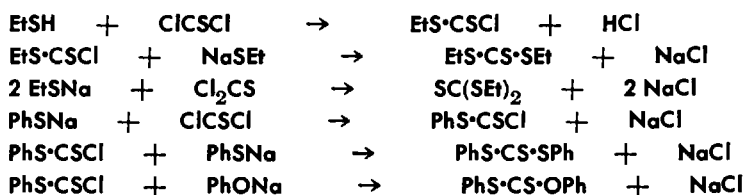


This acid melts at 110° and is only slightly soluble in cold water.^{788c} α -Bromostearic acid forms a trithiocarbonate.¹⁶⁸⁸

An aromatic trithiocarbonate can be made from a diazonium salt: ²⁵⁷



Thiophosgene reacts with a mercaptan in two stages, or with a mercaptide in one: ^{38, 737, 805, 934a}



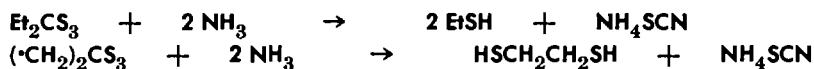
The chloride $\text{PhS}\cdot\text{CSCl}$ is a heavy red oil which reacts with thiophenol, phenol, and amines. Phenyl trithiocarbonate, Ph_2CS_3 , melts at 95.7° , while the oxygen compound, Ph_2CO_3 , melts at 79.5° .^{1385b} As the reaction goes in two stages and a different mercaptan can be employed in the second, the synthesis of a variety of mixed trithiocarbonates, $\text{RS}\cdot\text{CS}\cdot\text{SR}'$, is possible. The difficulty of obtaining thiophosgene has limited the exploitation of these reactions. As will appear in a following section, mixed trithiocarbonates can be prepared in other ways.

The absorption spectrum of ethyl trithiocarbonate shows a band which suggests a cyclic structure, a double bond between the two thiol sulfur atoms.¹³¹⁷ The spectrum of the ester is similar to that of the acid but different from that of the salts.⁷⁰⁵ The absorption spectra of several xanthates, sodium ethyl trithiocarbonate, and sodium trithiocarbonate have been compared.^{47c} Ultraviolet and infrared spectra have been used to study the structure of several trithiocarbonates.²⁶⁹

Methyl trithiocarbonate can be prepared by the reaction of dimethyl sulfate on a mixture of carbon disulfide and potassium hydroxide.⁷⁵³

Reactions of Alkyl Trithiocarbonates

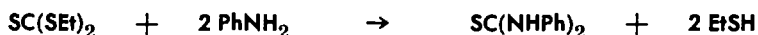
Ammonia, in alcohol solution, displaces the mercaptans from ethyl and ethylene trithiocarbonates and forms ammonium thiocyanate.



The expected product, thiourea, may have rearranged to the more stable ammonium thiocyanate.^{814a, 814d} *i*-Butyl trithiocarbonate reacts similarly with ammonia.^{1203b} With a limited amount of ammonia the reaction may stop half way:⁴¹⁷



When ethyl trithiocarbonate is heated with aniline to 160°, or refluxed with it in alcoholic solution, the mercaptan is displaced: ^{814d, 1710a}

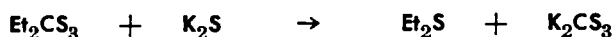


With a secondary amine the reaction goes no farther than the thiourethane, $\text{R}_2\text{N}\cdot\text{CS}\cdot\text{SR}'$, regardless of the proportions.⁴¹⁷ Boiled with aniline it loses all of its sulfur: ^{1710b}



In alcohol solution the reaction does not go so far.^{814d, 1710b}

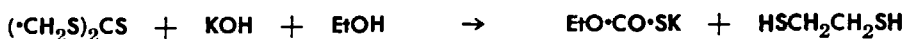
Heated with potassium sulfide, ethyl trithiocarbonate is decomposed: ¹⁴⁷³



In alcoholic potash, ester interchange and saponification take place: ^{1412b}



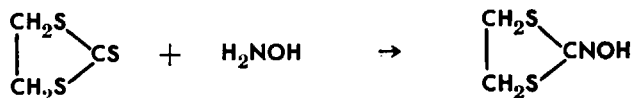
Ethylene trithiocarbonate reacts similarly: ⁵⁶⁸



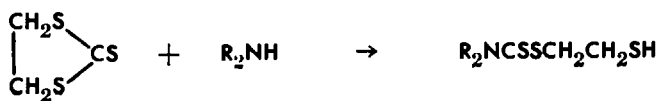
By the same reagents phenyl trithiocarbonate is converted to potassium xanthate, $\text{KS}\cdot\text{CS}\cdot\text{OEt}$.²⁵⁷ Ethylene trithiocarbonate can be oxidised by dilute nitric acid to the dithiocarbonate: ^{269, 814c, 1163}



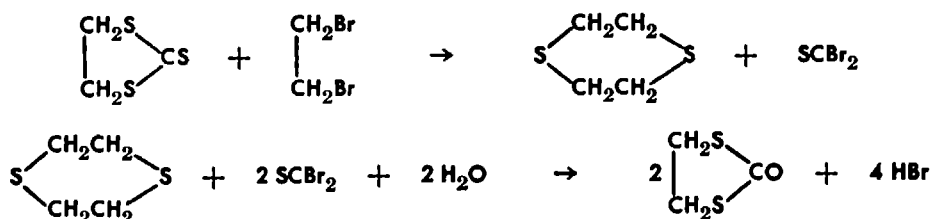
It reacts with hydroxylamine: ¹¹⁶³



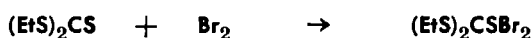
With a secondary amine a dithiocarbamyl mercaptan is formed: ⁴⁰⁵



Ethylene trithiocarbonate and ethylene bromide give dithiane which is converted into ethylene dithiocarbonate by thiocarbonyl bromide: ^{814c}



Ethyl ⁹³ and ethylene ²⁶⁹ trithiocarbonate take up bromine:



Uses

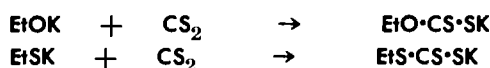
Ethyl trithiocarbonate ⁴⁵⁸ and the ethyl sodium salt, $\text{EtS}\cdot\text{CS}\cdot\text{SNa}$, ⁴²⁴ are said to be useful in flotation. Sulfenyl trithiocarbonates have been used as flotation agents. ^{39b} Glycol and glycerol esters are said to improve the wet strength of viscose yarns. ^{1023a} Derivatives of thiocarbonic acids are claimed as vulcanization accelerators. ^{39b, 225b, 225c} They may be used in protein glues. ¹⁰ Alkylene trithiocarbonates are useful for improving plywood adhesives. ⁸⁵⁴

A rather high concentration of methyl trithiocarbonate killed only 20% of rice weevils in 24 hours. ¹³⁶⁸ Certain trithiocarbonates have been used as plant defoliants, ⁶⁴³ and others as pesticides. ^{39b, 72}

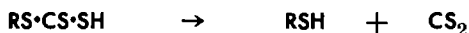
Trichlorobenzyl trithiocarbonate, $(\text{Cl}_3\text{C}_6\text{H}_2\text{CH}_2\text{S})_2\text{CS}$, which is made by reacting trichlorobenzyl chloride with the sodium salt of the acid, is claimed as an addition to lubricating oils to be used under extreme pressure conditions. ^{130a} The trithiocarbonate from α -bromostearic acid is a rust inhibitor. ¹⁶⁸⁸ Various trithiocarbonates are useful as lubricating oil additives. ^{39b, 1052} Esters of thiocarbonic acid have been patented for use in hair waving solutions. ^{419, 748} The thioglycolic acid ester, $\text{SC}(\text{SCH}_2\text{COOH})_2$, is among those discussed. ^{419, 744} This ester is also a modifier in bulk styrene polymerization. ¹²⁹⁰

ESTER SALTS OF TRITHIOCARBONIC ACID

Carbon disulfide reacts with potassium mercaptide as it does with the alcoholate: ^{271a, 271b, 786b}



The acids, $\text{RS}\cdot\text{CS}\cdot\text{SH}$, are strong but unstable. K for $\text{EtS}\cdot\text{CS}\cdot\text{SH}$ is 2.8×10^{-2} .⁷¹⁸ Like the corresponding xanthic acids, the free acids decompose readily:



Carbon disulfide and sodium hydroxide are added to ethyl mercaptan. The excess of carbon disulfide is removed and the salt recrystallized from a mixture of alcohol and ether.^{47b} *i*-Butyl,^{1203b} *t*-butyl,⁶⁸ dodecyl,⁵⁶⁷ and benzyl^{68, 756} mercaptans react similarly with carbon disulfide and alkali. Ethyl, butyl, or other mercaptans, react with carbon disulfide and concentrated aqueous alkali.^{125b} *t*-Butyl mercaptan and its homologs up to eleven carbon atoms react with carbon disulfide and sodium hydroxide in *i*-propyl ether. These salts are ore flotation agents and intermediates for insecticides and therapeutics.³⁶⁴

An equimolecular mixture of carbon disulfide and thioglycolic acid with an excess of aqueous potassium hydroxide, yields the salt $\text{KS}\cdot\text{CS}\cdot\text{SCH}_2\text{COOK}$. Chloracetic acid converts this to the trithiocarbonate, $\text{SC}(\text{SCH}_2\text{COOH})_2$. The acid $\text{EtS}\cdot\text{CS}\cdot\text{SCH}_2\text{COOH}$ melts at 76° .^{786c} A cuprous mercaptide and carbon disulfide unite: ⁴⁷⁷



Lead trithiocarbonates can be formed from lead mercaptides and carbon disulfide.⁷³⁵

Methylene mercaptan resulting from the reduction of carbon disulfide, reacts with unchanged carbon disulfide and alkali: ¹¹⁶⁵

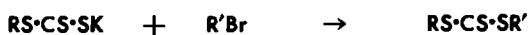


Ethylene trithiocarbonate for flotation is said to be obtained from glycol, ethylene chlorhydrin, or chloride, and carbon disulfide in the presence of an alkali.^{322, 1237c}

An ester of trithiocarbonic acid is obtained readily by the reaction of the alkali ester salt with an alkyl halide:



This is useful for making trithiocarbonic esters in which the two alkyls are different:



Thus potassium ethyl trithiocarbonate and ethylene bromide react: ^{1699b}



The salt, $EtS \cdot CS \cdot SK$, gives precipitates of the lead, mercury, and silver salts with the ions of these metals. As is the case with the xanthate, the copper salt is the cuprous:



The salts decompose on heating leaving metal sulfides. ^{271b} The lead salt decomposes on standing: ⁷³⁵

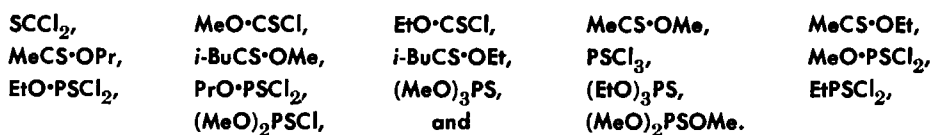


The disulfide formed by the reaction with copper sulfate is also formed by oxidation with iodine ¹⁶³⁸ or hypochlorous acid. ³⁶⁶ Electrolysis of potassium ethyl trithiocarbonate leads to the disulfide, $EtS \cdot CS \cdot S \cdot CS \cdot SEt$, a yellow oil. ¹⁴²⁹ With sulfur, mono- or dichloride, tri- or tetra-sulfides are formed. The monosulfide, $(EtSCS)_2S$, is the product of the reaction of a salt with the ester of dithiochloroformic acid. ¹⁶³⁸ When heated the sodium salt gives off a mixture of oils. ³¹²

The spectra of trithiocarbonate ester salts have been studied. ⁶⁸

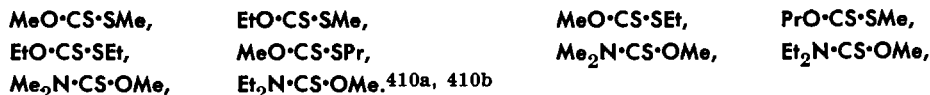
Phosphorescence or Oxyluminescence of Organic Sulfur Compounds

When the vapors of certain organic sulfur compounds come in contact with oxygen, phosphorescent light is emitted. Compounds which contain doubly bound sulfur as in thioncarbonates or thion-acetates and thion-phosphates show this phenomenon. Some of these are: ^{413d, 414a}



The ester, $MeO \cdot CS \cdot SMe$, is strongly phosphorescent and the ethyl ester, $EtO \cdot CS \cdot SMe$, is slightly less so while the dimethylurethane, $MeO \cdot CS \cdot NMe_2$, is only feebly so. ¹³⁵

To show this effect it is, of course, necessary for a compound to have an appreciable vapor pressure at ordinary temperatures. For compounds of a given type the activity decreases as the molecular weight increases. The luminosity decreases for the following compounds in the order given:



This autoxidation is remarkable in that only a minute proportion of the vapor that is present takes part, even in the presence of a large excess of air. It ceases immediately and permanently if the mixture is sealed up. A compound that has glowed and fumed shows the same phenomenon repeatedly when exposed to successive portions of fresh air. The partial pressure of oxygen required is different for different compounds, 5 mm. for SCCl_2 or MeCS_2OMe , 7 mm. for $\text{MeO}\cdot\text{CS}\cdot\text{SMe}$, and 25 mm. for $\text{Me}_2\text{N}\cdot\text{CS}\cdot\text{OMe}$. The oxyluminescence is favored by the presence of ammonia and alkalies and hindered by that of ether, acetaldehyde, turpentine, acetone, and pyridine. Sulfur dioxide and trioxide are produced.^{411b, 414c} The small extent of the oxidation in a confined volume of oxygen was strikingly shown by an experiment in which 1 g. each of $\text{MeS}\cdot\text{CS}\cdot\text{SMe}$, $\text{MeCS}\cdot\text{OEt}$, $\text{SP}(\text{OMe})_3$, SPCl_3 , $\text{Me}_2\text{N}\cdot\text{CS}\cdot\text{OMe}$, and $\text{MeO}\cdot\text{CSCl}$ was sealed up with 30 cc. of oxygen or air. After twenty-six years the tubes were opened and the disappearance of oxygen determined. This varied from none to 8 cc. The maximum amount could not have accounted for more than 3% of the compound present.^{411c} In the presence of two moles of ammonium hydroxide to one of the compound the oxidation is rapid and extensive, 70 to 85% for $\text{EtO}\cdot\text{CS}\cdot\text{SEt}$, $\text{MeO}\cdot\text{CS}\cdot\text{SMe}$, $\text{MeO}\cdot\text{CS}\cdot\text{OMe}$, $\text{MeO}\cdot\text{CSCl}$, and $\text{EtO}\cdot\text{CSCl}$. For $\text{EtO}\cdot\text{CS}\cdot\text{OEt}$ and SCCl_2 it was slower and only 30% complete.^{118c, 122} The whole subject has been reviewed by Delepine.^{411d}

It has been found by others that dimethyl trithiocarbonate does not give white fumes if it is pure and dry. The phosphorescence is attributed to triboluminescence influenced by moisture and pressure, and it is assumed that saponification precedes the fuming.^{245a, 753}

Physical Properties of Thiocarbonic Acid Derivatives

The object is to give physical properties, as far as known, of a number of compounds with references to their preparation. No claim is made as to completeness.

As has been said in previous volumes, attention is called to the incompleteness and doubtful accuracy of the data and to the desirability of more accurate measurements.

Reference must be made to three general articles: A study of spectra at different temperatures of $(\text{PhO})_2\text{CS}$, $(p\text{-MeO-C}_6\text{H}_4\text{O})_2\text{CS}$, and $(\text{PhS})_2\text{CS}$,¹⁶⁷ a survey of the molecular refractivity of sulfur compounds, including S_2 in xanthates and S_8 in trithiocarbonates,¹⁵⁸ and a study of refractivities at 20° , densities and surface tensions over a range of temperatures and parachors of a number of dialkyl xanthates, bond refractions and bond parachors and bond-refraction coefficients for a number of links, with measurements of refractive indices at 20° for the C, D, F, and G lines.¹⁶⁶

ACID CHLORIDES

$\text{MeS}\cdot\text{CO}\cdot\text{Cl}$, b. 110° .³⁸

$\text{EtS}\cdot\text{CO}\cdot\text{Cl}$, b. 136° ; ^{415b, 1413a} d 16/4 1.184.^{1413a}

$i\text{-PrS}\cdot\text{CO}\cdot\text{Cl}$, b. $133\text{--}5^\circ$.¹⁸⁶

$i\text{-AmS}\cdot\text{CO}\cdot\text{Cl}$, b. $190\text{--}5^\circ$, 193° ; d 17.5/4 1.076.¹⁴⁶²

$\text{PhS}\cdot\text{CO}\cdot\text{Cl}$, liq. at -18° ; ^{1365b} b_8 $95\text{--}7^\circ$, ³⁵⁹ b_{13} 104° , b_{22} 150° , b_{724} $225\text{--}7^\circ$; d 1/4 1.285.^{1365b}

$\text{PhCH}_2\text{S}\cdot\text{CO}\cdot\text{Cl}$, b_{18} 133° .¹⁸⁶

Chaulmoogryl $\text{S}\cdot\text{CO}\cdot\text{Cl}$, $b_{1.0}$ $200\text{--}3^\circ$.^{998a}

$\text{MeO}\cdot\text{CS}\cdot\text{Cl}$, b. 108° , ^{411a, 414a, 414b, 415b} d 0/4 1.2975,^{411a} d 22/4 1.2686,^{411a} d 23.5/4 1.2666; n 23.5/D 1.49828.^{415b}

$\text{EtO}\cdot\text{CS}\cdot\text{Cl}$, b. 136° ,^{52, 934a} 128° , ^{411a, 414a, 415b} 127° ; ¹³⁶⁶ d 0/4 1.2138,^{411a} d 15/4 1.1955,^{411a} 1.195,^{415b} d 17.5/4 1.1925; ^{415b} temp. coef. of thermal decompn. 3.2 at $77\text{--}90^\circ$, 2.2 at $90\text{--}8^\circ$.¹⁰⁶

$\text{PrO}\cdot\text{CS}\cdot\text{Cl}$, b. $148\text{--}51^\circ$.^{411a}

$\text{PhO}\cdot\text{CS}\cdot\text{Cl}$, m. -0.5° ; ^{1365a} $b_{0.5}$ 90° ,¹⁸ b_{10} 91° , b_{15} 100° ; d 17/4 1.283.^{1365a}

$\text{C}_{10}\text{H}_7\text{O}\cdot\text{CS}\cdot\text{Cl}$, $\alpha\text{-}b_{13}$ $165\text{--}6^\circ$; $\beta\text{-m.}$ 77° .¹³⁶⁶

$2,4,6\text{-Cl}_3\text{C}_6\text{H}_2\text{O}\cdot\text{CS}\cdot\text{Cl}$, b_{12} $146\text{--}7^\circ$.^{1460b}

$\text{MeS}\cdot\text{CS}\cdot\text{Cl}$, b_{15} $50\text{--}2^\circ$.³⁸

EtS·CS·Cl, m. $< -40^\circ$; ⁸⁰⁵ b_{10} $90-110^\circ$, ^{171b} b_{15} $74-5^\circ$, b_{19} 81° , ⁸⁰⁵ b_{34} 110° , ¹²⁷ $b_{vac.}$ 100° , b. 240° ; d_{16} 1.1408.^{935a}
 $C_{12}H_{25}S\cdot CS\cdot Cl$, b_{1-5} $176-8^\circ$; n 20/D 1.5196.¹²⁷
 $PhS\cdot CS\cdot Cl$, b_{15} 135° ; d 15/4 1.331.^{1365b}

ACID ANHYDRIDES

$(EtOCO)_2S$, oil; ¹⁷²² b_{22} 118° , ^{786a} b. 180° ; ¹¹⁴⁰ d 20/4 1.123.^{786a}
 $(EtOCO)_2Se$, m. 127° .^{1160b}
 $EtOCS\cdot S\cdot COOEt$, b_{18} 133° , b_{50} 149° ; d 20/4 1.180; n 20/D 1.527.^{786a}
 $BuOCSSCOOBu$, b_{12} $120-6^\circ$.⁵²²
 $(MeOCS)_2S$, m. 56° , ¹⁷⁹⁶ 55° .^{1540a, 1540c, 1722}
 $(EtOCS)_2S$, m. 55° , ^{1540a, 1540c, 1699b} 54° , ^{1735, 1796} 52.5° , ²⁴¹ 52° .¹⁷²²
 $(PrOCS)_2S$, m. 55° ; ^{1540a, 1540c, 1721c} $b_{0.5}$ 136° , ¹⁷²² $b_{2-2.5}$ $136-8^\circ$.¹⁷⁹⁶
 $(i-PrOCS)_2S$, m. 55° .^{1721c}
 $(i-BuOCS)_2S$, oil; d_{22} 1.126.¹⁷²²
 $(HexOCS)_2S$, n 25/D 1.5410.²⁴¹
 $(c-HexOCS)_2S$, m. 78° .¹⁷⁹⁶
 $(PhCH_2OCS)_2S$, m. 82.5° .^{241, 1796}
 $(menthylOCS)_2S$, m. 149° ; ^{297a, 1575} D m. 148° ; $[\alpha]_D$ $+46.42$.^{298c}
 $(EtOCH_2CH_2OCS)_2S$, n 25.5/D 1.15561.²⁴¹
 $PhC(:NPh)S\cdot CS\cdot OEt$, m. 98.5° .^{295c}
 $PhC(:NPh)S\cdot CS\cdot OCH_2Ph$, m. 73° .^{295c}
 $PhC(:NPh)S\cdot CS\cdot O$ menthyl, m. 106° .^{295c}
 $PhC(:NPh)S\cdot CS\cdot O$ bornyl, m. 88° , ^{295c} 117° .¹⁴⁸⁷
 $PhC(:NPh)S\cdot CS\cdot O$ fenchyl, m. 85° .^{295c}
 $PhC(:NC_6H_4Me-o)S\cdot CS\cdot OEt$, m. 77° .^{295c}
 $PhC(:NC_{10}H_7)S\cdot CS\cdot OEt$, α -m. 142° ; β -m. 124° .¹³⁶⁶
 $PhC(:Npseudocumyl)S\cdot CS\cdot OEt$, m. 97° .^{295c}
 $(EtO)_2PS\cdot S\cdot CS\cdot OEt$, b_1 $85-7^\circ$.⁷⁷

DIXANTHOGENS

$(MeOCSS)_2$, m. 23.5° , ^{213b, 241} 23° , ^{529, 1795b} $b_{0.1}$ $90-4^\circ$, ^{213b} b. 122° , ^{1327c} 154° ; ¹⁷⁹¹ d 1.180, ^{1327c} 1.17 ¹⁷⁹¹ d 30/4 1.3807; n 30/D 1.6715; MR 58.20.⁵²⁹
 $(EtOCSS)_2$, m. 32.5° , ^{213b} 32° , ^{529, 1393} 28° ; ^{147, 1210, 1536, 1795a} $b_{0.5}$ $107-9^\circ$, ^{213b} b. 210° , $210-2^\circ$; d_{18} 1.0703, ^{1790d} d 24.8/4 1.26043, ^{415b} d_{30} 1.265; ^{1795a, 1795b} n 24.8/D 1.62417.^{415b}
 $(ProOCSS)_2$, b. 117° ; d 1.087, ^{1327c} d 26.2/4 1.1966; ^{415b, 1210} n 26.2/D 1.60037.^{415b, 1210}

- (*i*-PrOCSS)₂, m. 57°; ^{331b}, ³³², ⁵²⁰ dipole moment 3.83.⁶⁹⁰
 (*i*-BuOCSS)₂, b. 165°; d 1.080.^{1327c}
 (*t*-BuOCSS)₂, m. 58°.³⁶⁶
 (AmOCSS)₂, b. 158°; d 1.007.^{1327c}
 (*i*-AmOCSS)₂, b. 187°.⁴²⁹
 (HexOCSS)₂, b₃ 170–5°; ²⁴¹ n 25/D 1.5569.²⁴¹
 (Neopentyl OCSS)₂, m. 68.5°.⁸⁶⁵
 (PhCH₂OCSS)₂, m. 56.5°,^{213b} 54.5°,²⁴¹ 54°; ^{1795c} d 1.218.^{1327c}
 (PhCH₂CH₂OCSS)₂, m. 50°,²⁴¹ 49.5°.^{1795c}
 (*p*-MeC₆H₄OCSS)₂, m. 72°.^{213b}
 (*p*-ClC₆H₄OCSS)₂, m. 91°.^{213b}
 (menthyl OCSS)₂, D m. 92.5°; L m. 93°; MR -1069.9 (C₆H₆),
 -1337.6 (EtOAc).^{297a}
 (bornyl OCSS)₂, D m. 83°; [α]_D +43.79; L m. 83°; [α]_D +44.12;
i-m. 82°.^{297b}
 (6-Me-bornyl OCSS)₂, m. 90.7°.²⁰⁶
 (MeOCH₂CH₂OCSS)₂, d 20/4 1.2891; n 20/D 1.5025; MR
 80.37.⁵²⁹
 (EtOCH₂CH₂OCSS)₂, n 25/D 1.575.²⁴¹
 (EtOCSS)₂S₂, m. 42°.¹⁵⁹⁹
 (EtOCSS)₂CS, m. 160° dec.¹⁷³⁵
 (MeSCSS)₂SO₂, m. 98°.⁶³⁰

ACIDS AND SALTS

- (MeO·CO·S)₂Hg, m. 93.5°.⁵⁹⁰
 (EtO·CO·S)₂Hg, m. 65°.⁵⁹⁰
 EtO·CO·SeH, m. 123°.^{1160b}
 2-Naphthalene-1-thiolcarbonate, m. 106°.¹⁵⁶⁴
 MeS·CO·SK, d_{15.2} 1.7002.³⁰⁷
 EtS·CO·SK, d_{18.2} 1.5564, d_{21.5} 1.5576, d₂₁ 1.558.³⁰⁷
i-BuS·CO·SK, d₁₅ 1.3718, d_{14.5} 1.3832.³⁰⁷
 MeO·CS·SH, dissoc. const. 0.034,⁷⁰³ K salt, m. 182–6; ¹⁴⁹³ 102–
 4°; ¹²¹² d_{15.2} 1.7002, 1.6754; ³⁰⁷ As salt, m. 130–50°; ^{1092c} Cr salt,
 m. 152°; ^{470b} Au salt, m. about 160°; ^{423b} Hg salt, m. 137°; ^{470b}
 MeHg salt, m. 59°; ⁹⁵⁷ Mo salt, m. 108°; ²⁶³ 100–20° dec.; ^{1092b}
 Pd salt, m. 140° dec.; ²¹³ *p*-MeOC₆H₄Te salt, m. 78°.^{561a}
 EtO·CS·SH, m. about -53°; ⁷⁰⁴ dissoc. const., 0.030,⁷⁰³ 0.028; ⁷¹⁸
 K salt, m. 226°; ¹⁴⁹³ d_{18.2} 1.5564, d₂₁ 1.558, d_{21.5} 1.5576; ³⁰⁷
 As salt, m. 94.8°; ¹⁵⁹³ Bi salt, m. 106°; ^{470b} Co salt, m. 119°; ⁴¹⁶
 117°; ^{470a} Cu salt, 2 forms I oil, b. 112°, II platelets, m.

- 72°; ^{1372b} Au salt, m. 168°; ^{423b} MeHg salt, m. 69°; EtHg salt, m. 53°; PrHg salt, m. 39°; ⁹⁵⁷ Mo salt, 118.5°, ^{1092b} 108° dec.; ²⁶³ Ni salt, m. 137°, ^{470b} 135°; ⁴¹⁶ Pd salt, m. 152°; ^{213d} Pt salt, m. 130°; ¹³²⁹ Ag salt, solubility product, 3.5×10^{-17} .¹²⁹¹
- PrO·CS·SH, guanidine salt, m. 113°; ¹¹⁰⁵ K salt, m. 233–9°, ¹⁴⁹³ 217°; ¹²¹² As salt, m. 42°; ^{1092c} Co salt, m. 60°; ⁴¹⁶ Mo salt, m. 89–91°; ^{1092b} Ni salt, m. 103°; ⁴¹⁶ Pd salt, m. 127°; ^{213d} Au salt, m. 167°. ^{423b}
- i*-PrO·CS·SH, K salt, m. 278–82°; solubility in acetone 6.0%; ¹⁴⁹³ Co salt, m. 159°; ⁴¹⁶ Au salt, m. 165°. ^{423b}
- BuO·CS·SH, K salt, m. 255–65°, ¹⁴⁹³ As salt, m. 38°; ^{1092c} Mo salt, m. 75°; ^{1092b} Ni salt, m. 89°; ⁴¹⁶ Au salt, m. 162–4°. ^{423b}
- i*-BuO·CS·SH, K salt, m. 260–70°; ¹⁴⁹³ d_{14.5} 1.3832, d₁₅ 1.3713; ³⁰⁷ As salt, m. 60°; ¹⁴⁹³ Co salt, m. 110°; ⁴¹⁶ Mo salt, m. 107.5°; ^{1092b} Ni salt, m. 119°; ⁴¹⁶ Au salt, m. about 162°. ^{423b}
- i*-AmO·CS·SH, K salt, m. 260–70°; ¹⁴⁹³ Mo salt, m. 121°; ^{1092b} Ni salt, m. 91°. ⁴¹⁶
- c*-HexO·CS·SH, As salt, m. 170° dec.; ^{1092c} Mo salt, m. 121° dec. ^{1092b}
- C₁₈H₃₇O·CS·SK, m. 206°. ¹²⁷
- PhCH₂O·CS·SH, m. 29°; ⁷⁰³ K salt, m. 180°; ¹⁴⁹³ Pd salt, m. 135°. ^{213d}
- HOCH₂CH₂O·CS·SK, m. 200–5°; solubility in acetone, 0.1%. ¹⁴⁹³
- MeOCH₂CH₂O·CS·SK, m. 216°. ¹⁴⁹³
- EtOCH₂CH₂O·CS·SK, m. 193–6°; solubility in acetone, 1.5%. ¹⁴⁹³
- PhOCH₂CH₂O·CS·SK, m. 178°. ¹⁴⁹³
- 2,4-Cl₂C₆H₃OCH₂CH₂O·CS·SK, m. 178°. ⁵⁴¹
- p*-ClC₆H₄OCH₂CHMeO·CS·SK, m. 222°. ⁵⁴¹
- 4,2-ClMeC₆H₃OCH₂CHMeO·CS·SK, m. 193–5°. ⁵⁴¹
- 2,4,5-Cl₃C₆H₂OCH₂CHMeO·CS·SK, m. 174°. ⁵⁴¹
- HOCH₂CH₂OCH₂CH₂O·CS·SK, m. 208°; solubility in acetone 0.4%. ¹⁴⁹³
- MeOCH₂CH₂OCH₂CH₂O·CS·SK, m. 145°; solubility in acetone 5%. ¹⁴⁹³
- 2,4-Cl₂C₆H₃OCH₂CH₂OCH₂CH₂O·CS·SK, m. 167–90°. ⁵⁴¹
- p*-ClC₆H₄OCH₂CH₂CH₂OCH₂CH₂CH₂O·CS·SK, m. 162–75°. ⁵⁴¹
- 2,4-Cl₂C₆H₄OCH₂CH₂CH₂OCH₂CH₂CH₂O·CS·SK, m. 172–8°. ⁵⁴¹
- HOCH₂CH₂OCH₂CH₂OCH₂CH₂O·CS·SK, m. 205°; solubility in acetone, 0.2%. ¹⁴⁹³
- (CH₂CH₂CH₂CH₂CH₂O·CS·SK)₂, m. 290°. ¹²⁷

K xanthate of triethanol amine, m. 214° ; solubility in acetone, 0.2%.¹⁴⁹³

HS·CS·SH, m. -30.5° ; d 17/4 1.47; parachor 197.3.¹¹⁵⁶

EtS·CS·SH, dissociation const. 2.8×10^{-2} ; ⁷¹⁸ K salt, m. 88.3° .^{47b}

ESTERS OF MONOTHIOACIDS

Thiol Esters

MeS·CO·OMe, b. 121° ,^{410b} 120° ; ^{415b} d 0/4 1.1452,^{410b} d 21/4 1.120,^{451b} d 21.5/4 1.1203,^{410b} d 23/4 1.1186; ^{415b} n 23/D 1.45242.^{410b, 415b}

EtS·CO·OEt, b. 156° ,^{1412b} $153-5^{\circ}$; ⁷⁵⁰ d 18/4 1.0285,¹²⁰⁹ d 18-19/4 1.0330,⁴⁹⁶ d 19/4 1.0285; ^{1412b} n 18-19/D 2.4601,⁴⁹⁶ n 18.2/D 1.4513,¹⁷³⁰ n 20/D 1.4513; molecular refractivity 35.13.¹³¹³

EtS·CO·OCH₂CHMe₂, b₁ $190-5^{\circ}$; d 20/4 0.9936; ^{1203b} n 18/D 1.4513.¹²⁰⁹

EtS·CO·OC₁₀H₇-β, m. 127° .¹⁵⁶⁴

i-BuS·CO·OEt, b. $190-3^{\circ}$; d 10/4 0.9935.^{1203b}

PhS·CO·OEt, m. 6° ; b₇₄₀ 253° , b₁₆ 130° , b₂₀ 135° .^{1365b}

PhS·CO·OPh, m. 56° ,^{1365b} 57° .^{1460a}

PhS·CO·OC₆H₄NMe₂, m. 84° ; MeBr, m. $85-98^{\circ}$.¹⁸⁶

PhCH₂S·CO·OC₆H₄NMe₂, MeBr, m. 149° .¹⁸⁶

p-MeC₆H₄S·CO·OC₆H₄Me-p, m. 109° .¹⁴⁶¹

PhCOCH₂S·CO·OEt, b_{1,2} 152° ; d 15/4 1.1948; n 15/D 1.554.⁶⁷⁵

EtOOCCH:CMes·CO·OEt, b₁₁ $148-50^{\circ}$.¹⁴³⁸

2-Benzoxazolyl S·CO·OMe, m. 141° .⁵⁹⁹

OC·OC₆H₄S, o, m. 26° ; b_{2.5} $93-6^{\circ}$.⁶⁶²

HORS·CO·O, resorcinol, m. 158° ; ^{886, 1707b} phloroglucinol, m. 181° .^{1708b}

CO(CH₂S·CO·OEt)₂, m. 46° .^{1403a}

(PhS·CO·OCH₂CH₂)₂O, d 20/4 1.248; n 20/D 1.5780.⁴³⁹

1,2-Me₂C₆H₂(S·CO·OH)_{2-3,5}, Me ester, b₁₄ 162° ; Et ester, b₁₄ $206-9^{\circ}$.¹²⁹⁹

Thion Esters

(MeO)₂CS, b. 120° ,^{410a, 410b, 414b} 119° ; ^{415b} d 0/4 1.13065,^{410b} d 15/4 1.1054,^{415b} d 17.4/4 1.1078,^{410a} d 24/4 1.1028,^{410b} d 24/4 1.103; ^{415b} n 15/D 1.46032,^{410a, 415b} n 24/D 1.45962.^{410b, 415b}

- $(\text{EtO})_2\text{CS}$, b. 161.5° ,¹³¹⁸ 162° ; ^{401c}, ^{1412b} d_{10} 1.032,^{401c} d 19/19 1.031,^{1412b} d 19/4 1.031,¹²⁰⁹ 1.0325 ^{1412b} d 17.5/4 1.0267,^{415b} d 18.2/4 1.0310; n 17.5/D 1.46012,^{415b} n 18.2/D 1.46010,^{415b}, ¹⁷³⁰ n 19/D 1.4610.¹²⁰⁹
 $(\text{PhO})_2\text{CS}$, m. 106° ; ¹⁸, ⁵², ⁴⁹¹ b. 336.40° .⁴⁹¹
 $(p\text{-MeC}_6\text{H}_4\text{O})_2\text{CS}$, m. 136° .¹⁴⁶¹
 $(\text{Me}_2\text{C}_6\text{H}_3\text{O})_2\text{CS}$, 2,4, m. 77.5° ; 2.6 m. 112° .¹⁸
 $(\text{ClC}_6\text{H}_4\text{O})_2\text{CS}$, *o*, m. 84.5° ; *p*, m. 158.5° .¹⁸
 $(2,4\text{-Cl}_2\text{C}_6\text{H}_3\text{O})_2\text{CS}$, m. 94.5° .¹⁸
 $(p\text{-BrC}_6\text{H}_4\text{O})_2\text{CS}$, m. 175° .¹⁸
 $(p\text{-NO}_2\text{C}_6\text{H}_4\text{O})_2\text{CS}$, m. 197° .¹⁸
 $(\text{MeOC}_6\text{H}_4\text{O})_2\text{CS}$, *o*, m. 69.5° ; *p*, m. 162° .¹⁸
 $(\beta\text{-C}_{10}\text{H}_7\text{O})_2\text{CS}$, m. 212° .⁵²
 $\text{MeO}\cdot\text{CS}\cdot\text{OEt}$, d 18/4 1.0643; n 18/D 1.45812.^{415b}
 $\text{EtO}\cdot\text{CS}\cdot\text{OPh}$, m. -17° ; b_{12} 124° , b_{17} 130° ; d 15/4 1.135.^{1365a}
 $\text{EtO}\cdot\text{CS}\cdot\text{OC}_{10}\text{H}_7\text{-}\beta$, m. 67° .¹³⁶⁶
 $p\text{-MeC}_6\text{H}_4\text{O}\cdot\text{CS}\cdot\text{OPh}$, m. 136° .¹⁸
 $\beta\text{-C}_{10}\text{H}_7\text{O}\cdot\text{CS}\cdot\text{OPh}$, m. 143° .¹⁸
 $p\text{-ClC}_6\text{H}_4\text{O}\cdot\text{CS}\cdot\text{OPh}$, m. 126° .¹⁸
 $p\text{-NO}_2\text{C}_6\text{H}_4\text{O}\cdot\text{CS}\cdot\text{OPh}$, m. 182° .¹⁸
 $p\text{-MeOC}_6\text{H}_4\text{O}\cdot\text{CS}\cdot\text{OPh}$, m. 104° .¹⁸
 $o\text{-O}_2\text{NC}_6\text{H}_4\text{O}\cdot\text{CS}\cdot\text{OC}_6\text{H}_3\text{Me}_2$, 2,6-m. 81° .¹⁸
bis-(Me 3,4-O-isopropylidene- β -D-arabinopyranoside)-2-thion-carbonate, m. 211.5° .⁵⁶²
 tetramethylene thioncarbonate, m. 156° .⁵⁵⁶

DITHIOCARBONIC ACIDS

Dithiol Esters

- $(\text{MeS})_2\text{CO}$, b. 169° ,^{414b}, ^{415b}, ⁴¹⁷, ¹⁴⁵⁰ 168° ; ^{408d} d 1.20,⁴¹⁷ d 17.5/4 1.191; n 17.5/D 1.55042.^{415b}
 $(\text{EtS})_2\text{CO}$, b_{19} $85\text{--}7^\circ$,^{213a} b. 196° ,^{408b}, ^{415b}, ^{1412b} 197° ,¹⁴⁵⁰ 194° ,^{415b} 191° ; ¹⁴⁸⁰ d 19/4 1.085,¹²⁰⁹, ^{1212b} d 23/23 1.084;¹⁴⁵⁰ n 18.2/D 1.5237,¹⁷³⁰ n 19/D 1.5168,¹²⁰⁹ n 20/D 1.5237.^{415b}, ¹²⁰⁹
 $(i\text{-AmS})_2\text{CO}$, b. 181° .¹⁴⁵⁰
 $(\text{PhS})_2\text{CO}$, m. 44° ,³⁵⁹ 43.5° ,¹⁴⁶⁷ 43° ,¹³¹⁸ 41° .^{1365b}
 $(\text{PhCH}_2\text{S})_2\text{CO}$, $b_{0.1}$ $166\text{--}72^\circ$.^{213a}
 $(\text{Ph}_2\text{CHS})_2\text{CO}$, m. 135.8° .^{114d}
 $(\beta\text{-C}_{10}\text{H}_7\text{S})_2\text{CO}$, m. 131° .¹⁸

- $(\text{PhCOCH}_2\text{S})_2\text{CO}$, m. 98° .⁸⁷⁵
 $\text{CO}(\text{SCH}_2\text{COOH})_2$, m. 156.6° ,^{114d} 156° ; ^{786a} electrical conductivity μ_∞ 378° ; $K = 0.156^\circ$; ^{786c} Et ester, m. 49.2° ,^{114d} 49° .^{786a}
 $\text{CO}(\text{SCH}_2\text{CH}_2\text{COOH})_2$, m. 116° , 109° .^{114d}
 Ethylene dithiolcarbonate, m. 39° ; ²¹⁸ 31° .^{814c}
 $\overline{\text{S}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{S}}\cdot\text{CO}$, *o*, *o'*-, m. 101.5° .⁶⁶
 $\text{MeS}\cdot\text{CO}\cdot\text{SAm-}i$, b. 140° .¹⁴⁶²
 $\text{MeS}\cdot\text{CO}\cdot\text{SCH}_2\text{CH}_2\text{NH}_2$, HCl, m. 156° .³⁵⁴
 $\text{MeS}\cdot\text{CO}\cdot\text{SC}_6\text{H}_7\text{Me}_4-2,2,6,6$, m. 56.5° ; b_{10} 158° ; d 20/4 1.0608; n 20/D 1.5363.⁹⁷³
 $\text{MeS}\cdot\text{CO}\cdot\text{S}$ fenchyl, b_{20} $171-3^\circ$; $[\alpha]$ 24/D -24.64 .⁹⁷³
 $\text{EtS}\cdot\text{CO}\cdot\text{SC}_6\text{H}_7\text{Me}_4-2,2,6,6$, b_{10} $167-9^\circ$; d 20/4 1.0305; n 20/D 1.5264.⁹⁷³
 $\text{PrS}\cdot\text{CO}\cdot\text{SC}_6\text{H}_4\text{Me}_4-2,2,6,6$, b_{10} $163-6^\circ$; d 20/4 1.0239; n 20/D 1.5241.⁹⁷³
 $i\text{-PrS}\cdot\text{CO}\cdot\text{SC}_6\text{H}_4\text{Me}_4-2,2,6,6$, b_{10} $171-3^\circ$; d 20/4 1.0114; n 20/D 1.5205.⁹⁷³
 $\text{PhCH}_2\text{S}\cdot\text{CO}\cdot\text{SCHMeNH}_2$, HCl, m. 123° .³⁵⁴
 $\text{PhCH}_2\text{S}\cdot\text{CO}\cdot\text{SCH}_2\text{CH}_2\text{NH}_2$, HCl, m. 179° ; formyl, m. 94° ; Ac., m. 83° .³⁵⁴
 $\text{PhCH}_2\text{S}\cdot\text{CO}\cdot\text{SCH}_2\text{C}_6\text{H}_4\text{Cl-}p$, m. 67.5° .^{213a}
 $\text{PhCH}_2\text{S}\cdot\text{CO}\cdot\text{SCH}_2\text{C}_6\text{H}_4\text{Me-}p$, m. 65° .^{213a}
 $\text{Ph}_2\text{CHS}\cdot\text{CO}\cdot\text{SCH}_2\text{COOH}$, m. 130.6° .^{114d}
 Me diacetone glucosyl-dithiolcarbonate, m. 142° .⁵⁷⁹

Xanthic Esters



R

- Methyl-, b. 167° ,¹³⁵ $410a$, $414b$, $415b$ 168° ,⁵³⁶ $1413b$ $170-2^\circ$,²²⁷ b_{20} 65° , b_{64} 89° ; ^{213a} d 0/4 1.2030,^{410a} d_{15} 1.143,²²⁷ d 16/4 1.1860,^{415b} d 18/4 1.174,^{1413b} d 18/4 1.184 ^{415b} d 25/4 1.1189; ⁴⁹⁶ n 16/D 1.57069,^{410a} 1.57039,^{415b} n 25/D 1.5462.⁴⁹⁶
 Ethyl-, b. 184° ,⁵⁸⁹ $1413b$ d 15/4 1.1330,^{415b} d_{18} 1.12; ^{1413b} n 15/D 1.55397.^{415b}
 Propyl-, b. $201-3^\circ$; d 0/4 1.10735, d 15/4 1.0931,^{410a} d 16.5/4 1.0917, d 20/4 1.0845, d 24.8/4 1.0841; ^{415b} n 16.5/D 1.54045,^{410a} ^{415b} n 20/D 1.53789, n 24.8/D 1.53554.^{415b}

3,2,5-Me (HO)O₂NC₆H₂CH₂-, m. 186°. ⁵²¹

EtO·CS·SCH₂COOH, m. 58°;^{786a} 54°;^{114b, 419} Me ester, b₂₄ 154°;^{786a} d 20/4 1.218; n 20/D 1.535; ^{786a} Et ester, b_{vac.} 165°;²⁶⁴ b₂₀ 157°; d 20/4 1.179; n 20/D 1.523; ^{786a} amide, m. 114°;¹⁶³⁴ anilide, m. 92°.⁷⁹²

EtO·CS·SCH₂CONHCOOEt, m. 104°.⁵⁷⁸

EtO·CS·SCH₂CONHCONH₂, m. 178°.⁵⁷⁸

EtO·CS·SCH₂CONHCONHMe, m. 185°.⁵⁷⁸

EtO·CS·SCHMeCOOH, m. 50°;^{114b} 49°;^{786a} [α]_D²⁰ +38.5;¹⁰⁰⁵ D m. 71°; [α]_D²⁵ -91.1; ^{572b} [α]_D²⁰ +55.51; molecular refraction +107.68; ¹⁰⁰⁵ L m. 70.5°; [α]_D²⁵ 92; ^{572b} Na salt, [α]_D²⁰ +20.86; molecular refraction +45.08.¹⁰⁰⁵

EtO·CS·SCH₂CH₂COOH, m. 71°;^{786a} 66°.^{114b}

EtO·CS·SCEtCOOH, m. 55°;^{114b} 60.5°;^{572a} D m. 32°; [α]_D²⁵ -92.9; L m. 32°; [α]_D²⁵ 92.8.^{572a}

EtO·CS·S(CH₂)₁₀COOH, m. 49°;³¹⁷ 38°;¹²⁷ 88° dec.; ⁷⁸ dodecylthio ester, m. 44°; decamethylene dithio ester, m. 49°; glyceroltriester, m. 45°.¹²⁷

EtO·CS·SCHPhCOOH, m. 90.5°.⁴⁵²

EtO·CS·SCH(CH₂Ph)COOH, m. 90°.¹¹⁷

EtO·CS·SCH(COOH)CH₂COOH, m. 150.5°;^{787c} 149°;^{114b} L m. 131°; [α]_D -94.8,^{788d} -92.6°; ^{787c} [α]_D 30.6 at 11-2°; 8.3 at 25°; -13.8 at 40-40.1°; ^{789a} D m. 131°; [α]_D¹⁷ +99.2°; ^{788d} [α]_D²⁰ +38.92; molecular refractivity +95.05; ¹⁰⁰⁵ mono Na salt, [α]_D²⁰ +16.87; molecular refraction, +43.86; di Na salt, [α]_D²⁰ +3.07; molecular refraction, +8.65.¹⁰⁰⁵

EtO·CS·SCH(COOH)CH₂CONH₂, m. 138°; [α]_D +65.6°; ^{787c} L m. 135°; [α]_D¹⁹ -53.4; D m. 133°; [α]_D¹⁷ 52.9.⁷⁹¹

EtO·CS·SCH₂CHO, m. 112°.⁶¹⁹

EtO·CS·S acetyl glyceraldehyde, m. 143°.⁶¹⁹

EtO·CS·S-D-glucose, m. 92.8°; [α]_D²⁰ -50.5; tetraacetyl compound, m. 89°; [α]_D²⁰ +30.8.¹⁴⁵⁵

EtO·CS·S triacetyl xylose, m. 106°; [α]_D²⁵ 17.30 (CHCl₃).⁶¹⁹

(EtO·CS·SCH₂)₂, m. 42°;^{1699b} 41°.^{1795c}

EtO·CS·SCH₂CHMeS·CS·OEt, d 20/4 1.1467.¹⁶²⁰

EtO·CS·SCH₂CMe₂S·CS·OEt, d 15/4 1.2486.¹⁶²¹

(EtO·CS·SCH₂)₂CH₂, d 0/0 1.238,^{1585b} d 20/4 1.1467,¹⁶²⁰ d 25/0 1.2146.^{1585b}

(EtO·CS·SCH₂CH₂)₂CH₂, d 0/0 1.158.^{1585b}

(EtO·CS·SCH₂CH₂CH₂)₂, m. 35°.¹²⁷

(EtO·CS·SCH₂CH:)₂, d 20/4 1.1829.¹⁶²⁰

(EtO·CS·SCH₂)₂CO, m. 78°. ^{1463a}

[EtO·CS·SCH(COOH)CH₂]₂CH₂, m. 135°. ^{1463b}

p-(EtO·CS·SCH₂)₂C₆H₄, m. 115°. ^{1795b}

PrO·CS·OR

Methyl-, b. 201–3.1°, ^{410a} b₇₄₉ 202.1–3.6°, ¹²¹⁰ b_{748.93} 202.1–3.6°; ¹⁴²⁵ d 0/4 1.10390, d 16/4 1.0883, ^{410a} d 20/4 1.0845, ^{415b} d 24.8/4 1.08409, ¹²¹⁰ 1.0841; ^{415b}, ⁴⁹⁶ n 24.8/D 1.53554, ^{415b}, ¹²¹⁰ 1.5355, ⁴⁹⁶ n 20/D 1.53789, ^{410a}, ^{415b}

Ethyl-, b₇₄₉ 215.6–7.6°, ¹²¹⁰ b_{748.93} 215.6–7.6°; ¹⁴²⁵ d 26.1/4 1.05054; ¹²¹⁰ n 26.5/D 1.5264, ⁴⁹⁶ n 26.1/D 1.52636, ^{415b}, ¹²¹⁰ d 26.5/4 1.0505. ⁴⁹⁶

EtOOCNHCOCH₂-, m. 94°. ⁵⁷⁸

H₂NCONHCOCH₂-, m. 169°. ⁵⁷⁸

MeNHCONHCOCH₂-, m. 176°. ⁵⁷⁸

i-PrO·CS·SMe, b₅ 65–8°, b₂₅ 86–9°, b₇₂₉ 175–9°; d 20/4 1.0777; n 21/D 1.5372. ^{1710b}

p-(PrO·CS·SCH₂)₂C₆H₄, m. 82°. ^{1795b}

C₄H₉O·CS·SR

BuO·CS·SCH₂CH:CHCH₂CH₂OMe, b₁₀ 170.8°; d₂₀ 1.0400; n 20/D 1.5220. ¹³¹⁶

(BuO·CS·SCH₂)₂, d 20/4 1.1214; n 20/D 1.5521. ^{1795c}

p-BuO·CS·SCH₂)₂C₆H₄, m. 50°. ^{1795b}

i-BuO·CS·SEt, b. 227–8°; d₁₇ 1.003. ^{1203a}

i-BuO·CS·Si-Bu, b. 247–50°; d₁₂ 1.009. ^{1203a}

i-BuO·CS·Si-Am, b. 265–70° with decomposition. ^{1203a}

p-(*i*-BuO·CS·SCH₂)₂C₆H₄, m. 50°. ^{1795b}

t-BuOCSSMe, b₆ 85–7°; d 20/4 1.0255; n 20/D 1.5242. ¹⁴⁷⁰

t-BuOCSSEt, b₅ 92.5°; d 20/4 1.0014; n 20/D 1.5206. ¹⁴⁷⁰

t-BuOCSSPr, b₈ 112–4°; d 20/4 0.9950; n 20/D 1.5122. ¹⁴⁷⁰

C₅H₁₁O·CS·OR

AmO·CS·SMe, b₁₀ 108.5°; d 20/4 1.040; n 20/D 1.5247. ¹⁷²⁷

AmO·CS·SCH₂C₆H₃(NO₂)OH-5,2, m. 180°. ⁵²¹

i-AmO·CS·SMe, b₁₀ 103°; d 20/4 1.036; n 20/D 1.5230. ¹⁷²⁷

i-AmO·CS·SAm-*i*, b. 265–70°. ^{1203a}

(*i*AmO·CS·SCH₂)₂, m. 35°; ⁹⁹⁶ d 20/4 1.1320; n 20/D 1.5610. ^{1795c}

(*i*AmO·CS·SCH₂)₂CH₂, oil. ⁹⁹⁶

(*i*AmO·CS·SCH₂CH₂)₂, m. 9°. ⁹⁹⁶

$(i\text{AmO}\cdot\text{CS}\cdot\text{SCH}_2\text{CH:})_2$, m. -9° .⁹⁹⁶
 $p\text{-(}i\text{AmO}\cdot\text{CS}\cdot\text{SCH}_2)_2\text{C}_6\text{H}_4$, m. 49° .^{1795b}
 $\text{MeEtCHCH}_2\text{O}\cdot\text{CS}\cdot\text{SEt}$, d 20/4 1.0167; $[\alpha]_D +6.32^\circ$; ^{295a} molecular refractivity $+12.12$.^{295a}
 $\text{Me}_3\text{CCH}_2\text{OCSSCH}_2\text{COOH}$, m. 61° ; amide, m. 92° ; Me amide, m. 50° ; di me amide, m. 59° .⁸⁶⁵
 $t\text{-AmO}\cdot\text{CS}\cdot\text{SMe}$, b₈ $110-2^\circ$; d 20/4 1.0235; n 20/D 1.5250.¹⁴⁷⁰
 $t\text{-AmO}\cdot\text{CS}\cdot\text{SEt}$, b₈ $118-20^\circ$; d 20/4 1.0160; n 20/D 1.5210.¹⁴⁷⁰

Higher Alkyl Xanthates

$\text{Me}_3\text{CCHMeOCSSMe}$, b₁₂ 100° ; d 18/4 1.0228.⁵⁵⁷
 $p\text{-(OctO}\cdot\text{CS}\cdot\text{SCH}_2)_2\text{C}_6\text{H}_4$, m. 50° .^{1795b}
 $p\text{-(}i\text{-OctO}\cdot\text{CS}\cdot\text{SCH}_2)_2\text{C}_6\text{H}_4$, m. 51° .^{1795b}
 $p\text{-(NonO}\cdot\text{CS}\cdot\text{SCH}_2)_2\text{C}_6\text{H}_4$, m. 41° .^{1795b}
 $\text{Me}_3\text{CCH}(\text{CMe}_3)\text{O}\cdot\text{CS}\cdot\text{SMe}$, m. 41° ; b₂₀ $141-3^\circ$.⁹⁷³
 $p\text{-(DecO}\cdot\text{CS}\cdot\text{SCH}_2)_2\text{C}_6\text{H}_4$, m. 50° .^{1795b}
 $\text{C}_{16}\text{H}_{33}\text{O}\cdot\text{CS}\cdot\text{SMe}$, m. 28.5° .¹⁶⁶²
 $\text{C}_{18}\text{H}_{37}\text{O}\cdot\text{CS}\cdot\text{SMe}$, m. 39° .¹⁶⁶²
 $\text{C}_{18}\text{H}_{37}\text{O}\cdot\text{CS}\cdot\text{SEt}$, 39° .¹²⁷
 $\text{C}_{18}\text{H}_{37}\text{O}\cdot\text{CS}\cdot\text{SC}_{18}\text{H}_{37}$, m. 54.5° .¹²⁷
 $\text{C}_{18}\text{H}_{37}\text{O}\cdot\text{CS}\cdot\text{SCH}_2\text{Ph}$, b₃ 160° .¹²⁷
 $\text{C}_{18}\text{H}_{37}\text{O}\cdot\text{CS}\cdot\text{S}(\text{CH}_2)_{10}\text{COOH}$, m. 78° ; dodecyl thioester, m. 55° ; decamethylene dithiol ester, m. 70° ; glycerol triester, m. 66.5° .¹²⁷
 $[\text{C}_{18}\text{H}_{37}\text{O}\cdot\text{CS}\cdot\text{SCH}_2(\text{CH}_2)_4\text{CH}_2]_2$, m. 56° .¹²⁷
 $c\text{-HexylO}\cdot\text{CS}\cdot\text{SCH}_2\text{COOH}$, m. 45° ; amide, m. 74.5° .¹⁶⁹³
 $(c\text{-HexylO}\cdot\text{CS}\cdot\text{SCH}_2)_2$, m. 75° .^{1795c}
 $p\text{-(}c\text{-HexylO}\cdot\text{CS}\cdot\text{SCH}_2)_2\text{C}_6\text{H}_4$, m. 59° .^{1795b}
 $2\text{-MeC}_6\text{H}_{10}\text{O}\cdot\text{CS}\cdot\text{SMe}$, b₁₈ $149-51^\circ$; d 15/4 1.083, d 20/4 1.0805; $[\alpha]_D -29.08$, -29.5 .¹¹⁰⁶
 $c\text{-Hexyl CH}_2\text{O}\cdot\text{CS}\cdot\text{SMe}$, m. 165° ,¹⁵ 17° .¹⁶⁶²
 $2,2,6,6\text{-Me}_4\text{C}_6\text{H}_7\text{O}\cdot\text{CS}\cdot\text{SMe}$, m. 60.5° ; b₁₀ $150-2^\circ$; d 20/4 1.0531; n 20/D 1.5355.⁹⁷³
 $2,2,6,6\text{-Me}_4\text{C}_6\text{H}_7\text{O}\cdot\text{CS}\cdot\text{SEt}$, b₁₀ 160° ; d 20/4 1.0175; n 20/D 1.5305.⁹⁷³
 $2,2,6,6\text{-Me}_4\text{C}_6\text{H}_7\text{O}\cdot\text{CS}\cdot\text{SPr}$, b₁₀ 158° ; d 20/4 1.0169; n 20/D 1.5264.⁹⁷³
 $2,2,6,6\text{-Me}_4\text{C}_6\text{H}_7\text{O}\cdot\text{CS}\cdot\text{SPr-}i$, b₁₀ $161-3^\circ$; d 20/4 1.0078; n 20/D 1.5250.⁹⁷³
 $2\text{-PhC}_6\text{H}_{10}\text{O}\cdot\text{CS}\cdot\text{SMe}$, *cis* m. 50° ; *trans* oil.¹⁶

- Allyl O·CS·SMe, b. 200–3°; d_{24} 1.1214.¹²⁴³
 Allyl O·CS·SEt, b. 210–2°; d_{28} 1.0690.¹²⁴³
 Allyl O·CS·S allyl, b. 221–3°.¹²⁴³
 PhO·CS·SPh, m. 51°.^{1365a}
p-MeC₆H₄O·CS·SCH₂Ph, m. 39.5°; $b_{0.1}$ 174–8°.^{213a}
 PhCH₂O·CS·SMe, m. 29.5°.¹⁶⁶²
 PhCH₂O·CS·SCH₂Ph, m. 42°; $b_{0.2}$ 176°.⁹⁹⁶
 PhCH₂O·CS·SCPh:NPh, m. 73°.^{295c}
 PhCH₂O·CS·SCH₂C₆H₄Me-*p*, m. 63°.^{213a}
 PhCH₂O·CS·SCH₂C₆H₄Cl-*p*, m. 63.5°.^{213a}
 PhCH₂O·CS·SCH₂COPh, m. 76.5°; 2,4-dinitrophenylhydrazone, m. 181°.⁴⁵²
 PhCH₂O·CS·SCHPhCOPh, m. 129°; 2,4-dinitrophenylhydrazone, m. 172°.⁴⁵²
 PhCH₂O·CS·SCH₂COCH₂Ph, m. 78°.⁴⁵²
 PhCH₂O·CS·SCH₂CONHCONH₂, m. 165°.⁵⁷⁸
 PhCH₂O·CS·SCH₂CONHCONHMe, m. 190°.⁵⁷⁸
 (PhCH₂O·CS·SCH₂)₂, d 20/4 1.1818; n 20/D 1.6160.^{1795c}
 (PhCH₂O·CS·SCH₂)₂CH₂, m. 62°.⁹⁹⁶
 (PhCH₂O·CS·SCH₂CH₂)₂, m. 71°.⁹⁹⁶
 (PhCH₂O·CS·SCH₂CH:) ₂, m. 60°.⁹⁹⁶
p-(PhCH₂O·CS·SCH₂)₂C₆H₄, m. 59°.^{1795b}
p-ClC₆H₄CH₂O·CS·SCH₂Ph, m. 49°; $b_{0.1}$ 186–91°.^{213a}
 (PhCH₂CH₂O·CS·SCH₂)₂, m. 86°.^{1795c}
p-(PhCH₂CH₂O·CS·SCH₂)₂C₆H₄, m. 68°.^{1795b}
 MePhCHCHMeO·CS·SMe, m. 78°; $[\alpha]_D^{25}$ 0.68.³⁴⁹
 (·CH₂CH₂O·CS·SCH₂Ph)₂, m. 76°.
 [·(CH₂)₅O·CS·SEt]₂, m. 50°.¹²⁷
 [·(CH₂)₅O·CS·SC₁₈H₃₇], m. 54°.¹²⁷
 HOOCCH₂O·CS·SEt, m. 78°; μ_∞ 378; $K = 0.212$.^{786c}
 HOOCCH₂O·CS·SCH₂COPh, m. 107°; Me ester, m. 76°.⁶⁷⁵
 HOOCCH₂O·CS·SCH₂COOH, m. 136°;^{419, 786a} Et ester, m. 35.^{786a}
 HOOCCH₂O·CS·SCH₂CONH₂, m. 142°,⁶⁷⁵ 130°.⁵
 (HOOCCH₂O·CS·SCH₂)₂CO, m. 181°.^{1463a}
 HOOCCHMeO·CS·SEt, active, m. 64°; D m. 36.7°; $[\alpha]_D$ -9.7°; solubility in water at 20°, 6.37 gm./liter;^{790b} DL m. 74°,^{790b} 72°; solubility in water at 20°, 3.67 gm./liter.
 HOOCHEtO·CS·SEt, D m. 32°; L m. 31.5°; racemic, Et ester, m. 59°.⁵⁷³

- HOOCCH₂CH(COOH)O·CS·SEt, m. 151°; ^{790a} $[\alpha]_D^{18}$ 28.2, $[\alpha]_D^{25}$ 36.6; ^{570b} solubility in water at 25°, 24.98 gm./liter. ^{790a}
- Bornyl O·CS·SMe, m. 57°; ¹²⁹⁴ L or D m. 57°; L $[\alpha]_D$ -33.38 (C₆H₆); -41.55 (EtOAc); D $[\alpha]_D$ +33.69 (C₆H₆), 41.45 (EtOAc); racemic, m. 29°; d 20/4 1.0923; n 20/D 1.54829. ^{297b}
- Bornyl O·CS·SEt, 53°; ⁴⁰ L or D m. 53°; $[\alpha]_D$ ±33.15 (toluene); racemic, m. 29°. ^{297b}
- Menthyl O·CS·SMe, m. 39°; ^{295b}, ^{297a}, ¹⁸⁶² molecular refractivity, -195.5 (C₆H₆), -198.6 (CHCl₃). ^{297a}
- Menthyl O·CS·SEt, m. 9°; d 21/4 1.0192; n 21/D 1.52761. ^{297a}
- Menthyl O·CS·SCH₂CONH₂, m. 98.9°. ⁷⁹³
- DL-Fenchyl O·CS·SMe, m. -18°; b₁₅ 156-60°; d 20/4 1.5756; n 20/D 1.54296; $[\alpha]_D^{20}$ -117.4; ¹³²³ $[\alpha]_D^{24}$ -138.28, ⁹⁷³ molecular refractivity 71.60. ¹⁸²³
- Thujyl O·CS·SMe, d 20/4 1.0569; n 20/D 1.53572. ^{297b}
- Pinocamphyl O·CS·SMe, m. 61°. ³⁰⁰
- β-pericyclo-camphanyl O·CS·SMe, m. 51°. ¹⁸¹
- Me glucoside O·CS·SMe, two isomers, α $[\alpha]_D^{22.8}$ 122.7; β m. 159°; $[\alpha]_D^{20}$ -5.01. ¹⁰²⁰
- Me-diacetoneglucose-3-Xanthate, m. 61°; b₁ 156-62°. ⁵⁷⁹
- Me 3,4-O-*i*-propylidene-β-arabinopyranoside O·CS·SMe, D m. 120°; $[\alpha]_D^{25}$ -217°; L m. 121° $[\alpha]_D^{25}$ 210; ¹⁷⁵⁸ corresponding Ph₃CS-ester, L m. 171°; $[\alpha]_D^{25}$ 54°. ¹⁷⁵⁸
- Me 4,6-O-benzylidene-3-O-Me-α-D-altropyranoside O·CS·SMe, m. 115°. ¹⁷⁵⁸
- 2-oxo-2-cholestanyl O·CS·SEt, m. 118°; $[\alpha]_D^{25}$ -64.5. ⁴⁵²
- cholesteryl O·CS·SMe, m. 128°; $[\alpha]_D$ -53; ¹²⁴⁰ m. 126° $[\alpha]_D$ -39°. ²⁹⁹
- cholesteryl O·CS·SEt, m. 144°; $[\alpha]_D$ -42. ¹²⁴⁰
- cholesteryl O·CS·SCH₂Ph, m. 143° $[\alpha]_D$ -30. ¹²⁴⁰
- cholesteryl O·CS·SCH₂C₆H₄Cl-*p*, m. 142.5°; $[\alpha]_D$ -29. ¹²⁴⁰
- cholesteryl O·CS·SCH₂C₆H₄OMe-*p*, m. 125°; $[\alpha]_D$ -28. ¹²⁴⁰
- cholesteryl O·CS·SCH₂C₆H₄NO₂-*p*, m. 148°; $[\alpha]_D$ -29. ¹²⁴⁰
- cholesteryl O·CS·SCH₂C₆H₃(NO₂)₂-2,4, m. 144° with decomposition. ¹²⁴⁰
- cholesteryl O·CS·SCHPh₂, m. 171.5°; $[\alpha]_D$ -25. ¹²⁴⁰
- cholesteryl O·CS·SCPh₃, m. 156.5°; $[\alpha]_D$ -21. ¹²⁴⁰
- Methylcholesteryl O·CS·SMe, m. 126°; $[\alpha]_D$ -39. ²⁹⁹
- $\overline{\text{SC}_6\text{H}_4\text{O}\cdot\text{CS}}$, *o*, m. 98°. ⁶⁶²

Sulfenxanthates

$\text{MeO}\cdot\text{CS}\cdot\text{S}(\text{SCCl}_3)$, b_{14} 144° ; d 20/4 1.5485; n 20/D 1.6310.⁵¹⁰
 $\text{EtO}\cdot\text{CS}\cdot\text{S}(\text{SCMe}_3)$, b_1 75° ; n 20/D 1.559.^{766a}
 $\text{EtO}\cdot\text{CS}\cdot\text{S}(\text{SCCl}_3)$, b_{14} 145° ; d 20/4 1.4751; n 20/D 1.6112.⁵¹⁰
 $\text{PrO}\cdot\text{CS}\cdot\text{S}(\text{SCCl}_3)$, b_1 131° ; d 20/4 1.4777; n 20/D 1.5995.⁵¹⁰
 $i\text{-PrO}\cdot\text{CS}\cdot\text{S}(\text{SMe})$, $b_{0.2-0.3}$ $50-2^\circ$.⁹³⁷
 $i\text{-PrO}\cdot\text{CS}\cdot\text{S}(\text{SCMe}_3)$, b_1 $94-7^\circ$; n 20/D 1.5468.^{766a}
 $i\text{-PrO}\cdot\text{CS}\cdot\text{S}(\text{SCCl}_3)$, b_1 130° ; d 20/4 1.4195; n 20/D 1.5970.⁵¹⁰
 $\text{BuO}\cdot\text{CS}\cdot\text{S}(\text{SCCl}_3)$, b_1 138° ; d 20/4 1.3876; n 20/D 1.5890.⁵¹⁰
 $i\text{-BuO}\cdot\text{CS}\cdot\text{S}(\text{SCCl}_3)$, b_1 136° ; d 20/4 1.3884; n 20/D 1.5860.⁵¹⁰
 $\text{AmO}\cdot\text{CS}\cdot\text{S}(\text{SCCl}_3)$, b_1 145° ; d 20/4 1.3580; n 20/D 1.5788.⁵¹⁰
 $i\text{-AmO}\cdot\text{CS}\cdot\text{S}(\text{SCCl}_3)$, $b_{0.7}$ 137° ; d 20/4 1.3452; n 20/D 1.5765.⁵¹⁰
 $\text{octyl O}\cdot\text{CS}\cdot\text{S}(\text{SCCl}_3)$, b_1 170° ; d 20/4 1.2578; n 20/D 1.5587.⁵¹⁰
 $\text{allyl O}\cdot\text{CS}\cdot\text{S}(\text{SCCl}_3)$, b_1 136° ; d 20/4 1.4971; n 20/D 1.6055.⁵¹⁰
 $c\text{-hex O}\cdot\text{CS}\cdot\text{S}(\text{SCCl}_3)$, d 20/4 1.4213; n 20/D 1.6120.⁵¹⁰
 $\text{PhCH}_2\text{O}\cdot\text{CS}\cdot\text{S}(\text{SCCl}_3)$, d 20/4 1.4396; n 20/D 1.6420.⁵¹⁰
 $\text{EtO}\cdot\text{CS}\cdot\text{S}(\text{SSCMe}_3)$, n 20/D 1.5942.^{766a}

TRITHIOCARBONATES

 $\text{RS}\cdot\text{CS}\cdot\text{SR}'$

dimethyl-, m . -3° ,²⁶⁹ -6.3° ;¹⁶¹⁴ b_5 $85-8^\circ$,^{1710b} b_{13} 92° ,²⁶⁹ b_{18} 111° ,^{1710a} b_{752} 207° ,²⁶⁹ b_{760} 220° ,^{1710a} b . 225° ,⁴¹⁷ $415b$ 224° ,⁵³⁸ 204.5° ,¹³⁶⁸ 205° ;²²⁷ d 0/4 1.2820,⁴¹⁷ d 17/4 1.2652,^{415b} d_{18} 1.159,²²⁷ d 20/4 1.2541, 1.2538,^{1710b} d 21/4 1.2630;^{415b}, ⁴¹⁷ n 15/D 1.6844,^{1710b} n 17/D 1.68554,^{415b} n 20/D 1.6740.^{1710b}
 diethyl-, m . -12° ;²⁶⁹ b_7 $102-4^\circ$,^{1710a} b_{10} 119° ,¹³¹⁸ b_{11} 113° ,²⁶⁹ b_{25} $145-7^\circ$,^{1710a} b_{34} 110° ,¹²⁷ b_{717} $241-4^\circ$,^{1710a} b_{760} 240° ,¹³¹⁸ b 240° ,⁷⁷, ^{814a}, ^{935a}, ¹²¹⁰, ^{1412b} $237-40^\circ$,^{401c} 188° ;¹⁰⁴³ d_{15} 1.012,¹²¹⁰ d 18.2/4 1.152,^{415b} d_{19} 1.152,^{1412b} d 18-19/4 1.1520;⁴⁹⁶ n 18-19/D 1.6201,⁴⁹⁶ n 18.2/D 1.6210.^{415b}, ¹⁷³⁰
 dibutyl-, b_4 $125-7^\circ$.⁷³⁵
 di-*i*-butyl-, b . $285-9^\circ$.^{1203b}
 di-*i*-amyl-, b . $245-8^\circ$; d 0.877.^{814c}
 didocecyl, m . 52.5° ,¹²⁷ 50° .⁵⁶⁷
 di-*c*-hexyl-, m . 76° .¹⁵³
 diallyl-, b . $170-5^\circ$; d 0.943.^{814c}
 $(\text{F}_3\text{CS})_2\text{CS}$, b . 110° .⁷³⁷

(MeCOCH₂S)₂CS, 2 crystal forms, needles, m. 59°, prisms, m. 74°. ^{790d}

(PhCOCH₂S)₂CS, m. 104°. ⁶⁷⁵

(HOOCH₂S)₂CS, m. 174°, ^{419, 786a} 173°, ⁵ 171°; ^{114c} μ_{∞} 378; K = 0.26; ^{786c} diamide, m. 207°, ⁵ 195–205° with decomposition; ^{786d} di(di Et amide), m. 120°; ¹⁴⁷¹ di Me ester, m. 32°; di Et ester, m. 47°. ^{786a}

(HOOCCH₂CH₂S)₂CS, m. 110°. ^{788c}

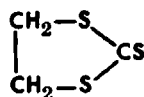
(PhS)₂CS, m. 43°, ¹³¹⁸ 95.7°, ^{1365b} 95°; ⁵² b₃₀ 210–5°; d 0/4 1.2668, d 20/4 1.2493. ²⁵⁷

(PhCH₂S)₂CS, m. 83°. ²⁴¹

EtS·CS·SC₁₂H₂₅, b₄ 116–8°; n 20/D 1.4872. ¹²⁷

t-BuS·CS·SCH₂Ph, b_{1.8} 220–3°. ⁷²

EtS·CS·SCH₂COOH, m. 76°; K = 0.082; amide, m. 124°, ^{786c} anilide, m. 98°. ⁷⁹²



Ethylene trithiocarbonate, m. 50°, 41°, ¹¹⁶³ 39°, ⁵⁶⁸ 37°, ^{372, 405} 36.5°; ^{814a} d 1.4768; ^{814a} MeI, m. 132°; AgNO₃, m. 124°; HgCl₂, m. 191°; 2 HgCl₂, m. 223°.

2-Methyl-, d 20/20 1.31. ^{814c}

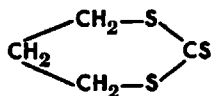
2-Phenyl-, m. 88°. ³⁷²

2-*p*-MeOC₆H₄OCH₂-, m. 69°. ⁷²

2-*p*-NO₂C₆H₄OCH₂-, m. 123°. ⁷²

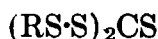
Tetramethyl-, m. 156°. ³⁷²

Cyclohexene trithiocarbonate, m. 169°. ³⁷²



Trimethylene trithiocarbonate, m. 80°; ¹¹⁵⁷ b₁₀ 157°. ²⁶⁹

3-Methyl-, m. 74°; phenyl hydrazone, m. 89°. ¹¹⁵⁷



Butyl-, d 20/20 1.1316; n 20/D 1.5928. ^{39b}

t-Butyl-, n 20/D 1.6005. ^{39a}

CHAPTER 3.

Thiocarbamic Acids and Derivatives

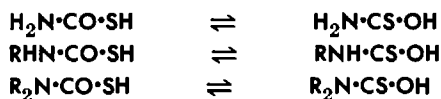
Monothiocarbamic Acids

INTRODUCTION

There are three classes of carbamic acids:



Corresponding to these there are three monothiocarbamic acids in which a sulfur atom replaces one of the oxygens. As one of these is in the carbonyl group and the other in the hydroxyl, there should be a thion- and a thiol-acid of each of the three classes but these are tautomeric:



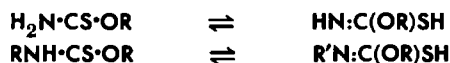
This statement actually applies to the salts, since the free acids can not be isolated. The salts are well known.

The tautomerism does not extend to the esters of which all six classes are known:



These can be distinguished as thiolurethans and thionurethans.

There is, however, another kind of tautomerism that does apply to the esters of two of these classes as it does to thioamides:



The salts have been considered as having the structures $\text{HN}\cdot\text{C}(\text{OR})\text{SK}$ and $\text{R}'\text{N}\cdot\text{C}(\text{OR})\text{SK}$. The alkylation products $\text{R}'\text{N}\cdot\text{C}(\text{OR})\text{SR}''$ are known^{1019b} and will be considered later.

PREPARATION OF SALTS

In general metal salts may be prepared by double decomposition. For example, the dimethylamine salt of dimethyl thiocarbamic acid yields amorphous precipitates with salts of copper, zinc, cadmium, and lead.¹²⁷⁰ Heavy metal salts, however, generally decompose to give the sulfide of the metal.

Carbon oxysulfide reacts with ammonia: 27a, 607, 961, 1104, 1447



In the early days there was much discussion as to the constitution of the salt, whether it is $\text{NH}_2\cdot\text{CO}\cdot\text{SNH}_4$ or $\text{NH}_2\cdot\text{CS}\cdot\text{ONH}_4$.^{310, 547} Evidence was brought forward for each of these tautomeric structures.

The equilibria in the reactions of carbon dioxide and of carbon oxysulfide with ammonia have been compared:



The pressures in atmospheres with which urea is formed are: ⁹³⁹

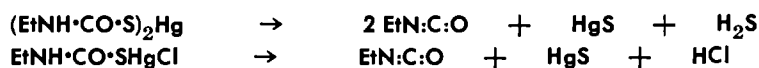
At	25°	100°	130°
From CO_2	0.00019	0.57	0.74
From COS	42.0	40000.0	300000.0

Urea can be produced commercially starting with carbon oxysulfide.^{567.5, 940}

Carbon oxysulfide combines with a primary amine: ^{33, 581, 701}



By double decomposition two mercury salts can be obtained, $(\text{EtNH}\cdot\text{CO}\cdot\text{S})_2\text{Hg}$ and $\text{EtNH}\cdot\text{CO}\cdot\text{SHgCl}$. These salts decompose on heating:



If water is present the salt, $(\text{RNH}\cdot\text{CO}\cdot\text{S})_2\text{Hg}$, goes to a symmetrical urea, $(\text{RNH})_2\text{CO}$.^{33, 581} A diamine forms an acid which on heating gives a fiber forming linear polymer:^{912, 1219}



Alkali may be substituted for half of the amine:^{887a}



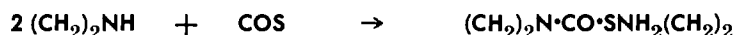
Carbon oxysulfide reacts with a secondary amine as well as or better than with a primary:^{887a, 1270}



Again alkali may be substituted for half of the amine:^{887a}

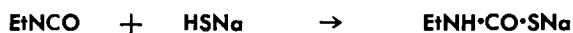


Ethylene imine may serve as the secondary amine:^{818a}



Piperidine and morpholine react similarly.¹²⁷⁰

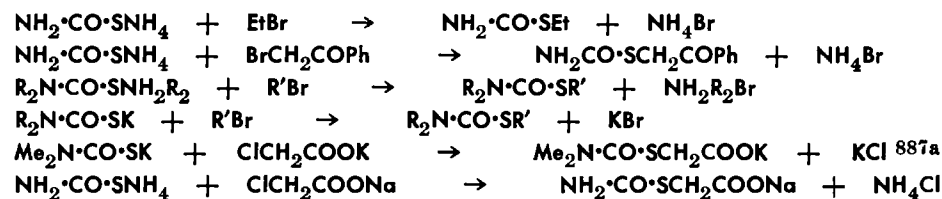
Sodium hydrosulfide adds to an isocyanate to form a salt of thiolcarbamic acid:⁸⁴⁴



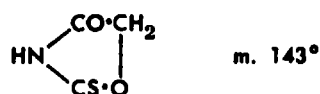
ESTERS OF THIOLCARBAMIC ACIDS

These are commonly called thiourethans, though the name is not a good one. There are three classes, $\text{H}_2\text{N}\cdot\text{CO}\cdot\text{SR}$, $\text{R}'\text{HN}\cdot\text{CO}\cdot\text{SR}$, and $\text{R}'_2\text{N}\cdot\text{CO}\cdot\text{SR}$, distinguished by the number of alkyls on the nitrogen.

A method of preparation that is applicable to those alkylated on the nitrogen as well as to the others is the alkylation of the thiocarbamate salts:^{547, 1104, 1453}



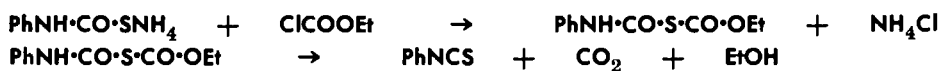
The free acid $\text{NH}_2\cdot\text{CO}\cdot\text{SCH}_2\text{COOH}$, melts at 139° and can be dehydrated to the cyclic imide:^{786d}



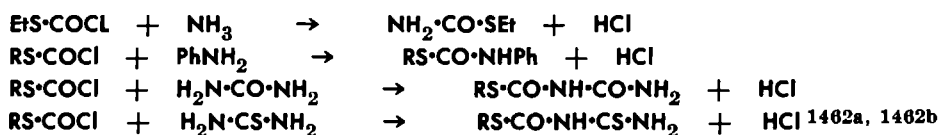
β -Propiolactone acts as a halide: 644c, 850b



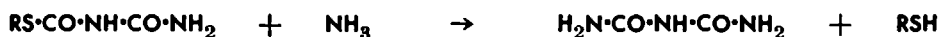
The reaction of ethyl chloroformate with phenylthiourethan probably follows the same course but the product is unstable and breaks up leaving a mustard oil: 27a



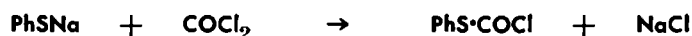
Another general method is the reaction of a thiochloroformic ester with ammonia or with an amine: 1413a



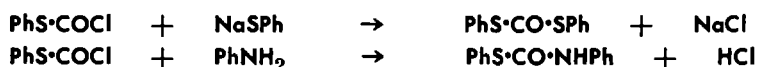
Biuret and mercaptan result from the action of ammonia on this urea derivative: 1276



Phenyl chlorothioformate is formed by the reaction of phosgene on sodium thiophenate:

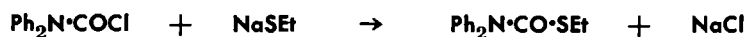


This chloride is an oil which may be used for the preparation of thiocarbonyl esters or of monothiourethans: 1365b, 1467



Other chlorothioformates may be employed.^{76, 998a, 998b} N-substituted thiocarbamic acid esters have been made from thiocarbonyl chlorides and amines.¹³⁵⁴ Phenyl chlorothioformate can be used to protect the amino group in peptide syntheses.^{498, 1027} The presence of an acid binding agent aids the reaction.⁷⁶

An ester of this type can be prepared from diphenyl carbamyl chloride and a mercaptide: 514

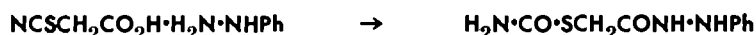


Tertiary amino mercaptans yield thiourethans when treated with a carbamyl chloride.^{1139, 1695, 1696a, 1696b}

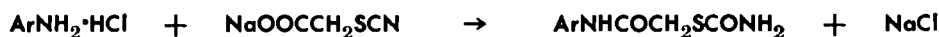
A special method for the unsubstituted thiourethan is the addition of water to a thiocyanate: ^{133, 327, 1297, 1413a}



The phenyl hydrazine salt of thiocyanoacetic acid is converted to carbamyl thioglycolic hydrazide; the water that is eliminated from one part of the molecule adds to the other: ⁵⁷⁶



The sodium salt reacts with an aqueous solution of an aromatic amine hydrochloride: ¹⁶⁹⁷



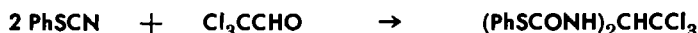
p-Phenetidine or ethylaniline, chloracetic acid, and ammonium thiocyanate give the same reaction.¹⁶³⁶ α -Thiocyanopropionic acid takes up water to form the carbamate of α -mercaptopropionic acid: ^{570a}



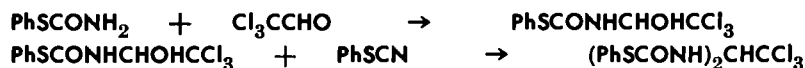
Hydrochloric acid causes the addition of water to a thiocyanate to form the thiocarbamate: ^{998a}



Gaseous hydrogen chloride passed into a dioxane solution of the thiocyanate brings about the same reaction.¹⁵⁸⁶ An alkyl thiocyanate kept in cold concentrated sulfuric acid is transformed into the corresponding thiocarbamate.^{1352a, 1352b, 1352c, 1356b, 1358, 1672} Phenyl thiocyanate reacts with chloral: ¹⁶⁷²

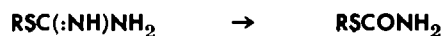


Or phenyl thiocarbamate may react with chloral to form an addition compound which with phenyl thiocyanate gives this product: ^{1352a}



This gives a precipitate with silver or lead ions.¹³⁵⁷

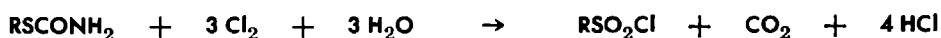
Oxidation of an isothioureia with hydrogen peroxide replaces the imino group by an oxygen: ^{998a, 998b}



When ethyl thiourethan is heated in a sealed tube to 150° it decomposes into a mercaptan and cyanuric acid. In the cold, hydrolysis takes place slowly unless alkali is present:



Chlorine passed into a water solution, kept below 10°, gives an almost quantitative yield of the sulfone chloride:



Bromine converts it to the sulfone bromide.^{75b} Alkyl thiocarbamates, treated with sodium plumbite, decompose to form lead mercaptides. This is a specific reaction for the alkyl thiol compounds.^{988b} Thiolcarbamylacetic acid heated above its melting point decomposes to give hydrocyanic acid and thioglycolic acid.¹²²¹

Mono-N-alkylthiourethans can be prepared by the addition of mercaptans to an isocyanate: ^{410b, 778c, 780d}

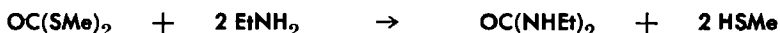


A novel synthesis of N-substituted thiocarbamates consists of treating an appropriate thiocyanate with an alcohol or olefin under acid conditions at 0–10°. ¹³⁵³ An alkyl thiocarbamate is one of four products of the reaction of 3-nitro-4-thiocyanatopyridine on aliphatic alcohols. ¹⁵⁸⁹

A special way to prepare N-dialkyl thiourethans is by the reaction of a secondary amine on a dithiocarbonic ester:



A secondary amine drives out only one molecule of the mercaptan while a primary goes further: ^{118b, 417, 787b, 1766}



The base catalyzed reaction of phenyl thiocarbamate or its mono-substituted derivatives with ammonia or with primary or secondary amines gives the corresponding substituted ureas. ³⁵⁹

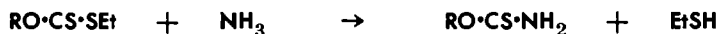
Ethyl thiolcarbamate gives abnormal values for freezing point lowering, while ethyl thioncarbamate gives normal values in freezing urethan. ²⁰⁵

ESTERS OF THIONCARBAMIC ACIDS

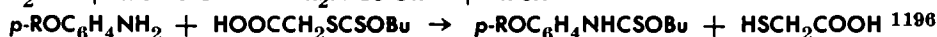
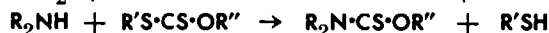
These also are of three classes according to the substitution on the nitrogen:



They may be called thiourethans, or more exactly, thionurethans, but are commonly known as xanthogenamides since they are prepared readily by the action of ammonia or an amine on xanthic esters: 15, 114b, 114c, 271a, 298a, 327, 401c, 568, 786c, 786d, 787b, 790c, 1203b, 1412b, 1413b, 1450, 1712a



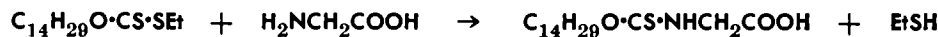
An amine is more efficient than ammonia in displacing the mercaptan: 118b, 135, 417, 593, 732a



Bornylxanthogenamide, $\text{C}_{16}\text{H}_{17}\text{O}\cdot\text{CS}\cdot\text{NH}_2$, m. 133° , $[\alpha] 20/\text{D} -2.9^\circ$,⁷⁹⁴ and 6-methylbornylxanthogenamide, m. 127° ,²⁰⁸ have been used for identification of the alcohols. The menthyl compound, $\text{C}_{10}\text{H}_{19}\text{O}\cdot\text{CS}\cdot\text{NH}_2$, is monoclinic.⁴¹ More complicated esters have been made in this way^{727d, 790b}



Glycine reacts with a xanthate:



Isolation of the xanthate is not necessary. A sodium alcoholate, carbon disulfide, and hydrazine give a thionocarbazate. The carbazates react with aldehydes to give hydrazones.¹⁸⁷⁸

Mono-N-alkyl thionurethans result from the addition of an alcohol to a mustard oil: 63, 289, 410b, 417, 451, 778c, 780d, 781a, 1454, 1712b, 1772

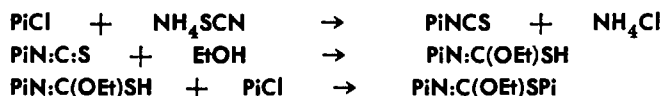


The ethyl ester is formed gradually in alcoholic spirits of mustard oil.¹²⁹⁸ A synthetic linear polymer is formed by the reaction of a dihydric alcohol or phenol and a di-isothiocyanate.^{259a} Ethyl DL-isothiocyanate propionate heated with alcohol gave the thiourethane, EtOOCCHMeNHCSOEt .^{874b} The reaction velocities of some sixty aryl isothiocyanates with ethanol have been compared.¹⁹⁹ It is preferable to use the alcohol as a sodium alcoholate: 157, 511, 1398, 1759



Acetoisothiocyanoglucose^{544b} and heptaacetyl isothiocyanolactose⁸⁷¹ react with alcohol to form thiourethans. It is claimed that cellulose thiourethan can be made by reacting alkali cellulose with an alkyl isothiocyanate.^{1023c}

Picryl chloride, ammonium thiocyanate, and alcohol react when they are heated together. Writing picryl chloride as PiCl , the following reactions may be written:



i-Propyl alcohol gives a small yield and *t*-butyl alcohol still less.^{356, 357}

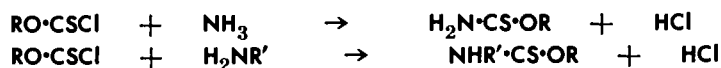
When sulfuric acid is added to a mixture of an alcohol and ammonium thiocyanate, a thionurethan is produced. The alcohol adds to the isothiocyanic acid:



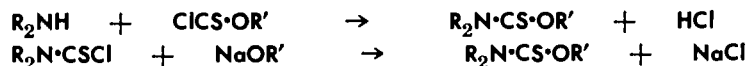
Some of the isomeric thiolurethan, $\text{H}_2\text{N}\cdot\text{CO}\cdot\text{SR}$, is also found but it is probable that it results from the isomerization of the thionurethan which is the chief product.^{133, 1332b} Heating in the presence of an acid converts the thion- into the thiol-.^{75a} This looks like a possible method of identifying alcohols.

The substituted urethan, $\text{EtO}\cdot\text{CO}\cdot\text{NH}\cdot\text{CS}\cdot\text{OEt}$, is obtained from ammonium thiocyanate and ethyl chloroformate in ethanol.^{201, 418, 684, 1716} Two isomeric forms of this have been isolated, the one melting at 44° and the other at 144° . They give different cyclic condensation products with ethylenediamine.⁶⁸¹ Potassium thiocyanate and benzoyl chloride refluxed in toluene and ethanol give ethyl benzoylthionocarbamate.¹⁵¹⁵ D-Glucose reacts with potassium thiocyanate in hydrochloric acid to form μ -thioglucosazoline which contains a thiocarbamyl group.⁴⁹⁴ The same salt can be used to introduce the thiocarbamyl group into 1-carbobenzoxypiperazine.⁶³⁷

The methyl, ethyl, and propyl chlorothioformates, $\text{RO}\cdot\text{CSCl}$, are pale yellow, oxyluminescent liquids.^{410b, 411a, 414a} These react with ammonia and with amines: ^{101, 410a, 411a, 415b, 1196, 1365a, 1413a}



Thiourethans in which the nitrogen is completely alkylated can be made from the above chloride or conversely from a dialkylthiocarbamyl chloride: ^{410a, 411a, 415b, 1196}



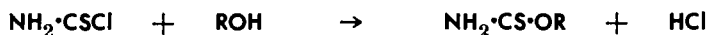
Rhodanurates react with sulfonated phenols to give sulfonated thioncarbamates: ¹⁵³⁹



With the free alcohol the reaction takes a different course; the anhydride is formed instead of the ester: ^{118a}



The ester, $\text{Et}_2\text{N}\cdot\text{CS}\cdot\text{OEt}$, oxidises spontaneously in the air.^{717b} Thiocarbamyl chloride reacts well with alcohols:

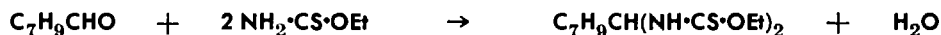


These thionurethans are solids.⁷⁴

Mono- and di-arylthioureas heated with alcohol and hydrochloric acid give alkyl-aryl thionocarbamates.^{1196, 1230}

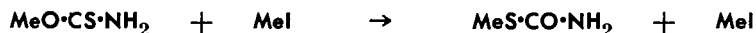
REACTIONS OF THIONURETHANS

Valeric aldehyde reacts with xanthogenamide, giving a compound melting at 108° : ¹²³

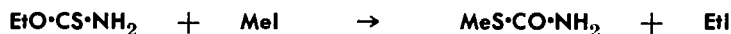


Xanthogenamide is readily acetylated to $\text{MeCONH}\cdot\text{CS}\cdot\text{OEt}$.^{29, 947c, 1714b}

When methyl thionurethan is kept with methyl iodide, a transformation takes place:



That the methyl iodide is not simply a catalyst is shown by an experiment with the ethyl ester:

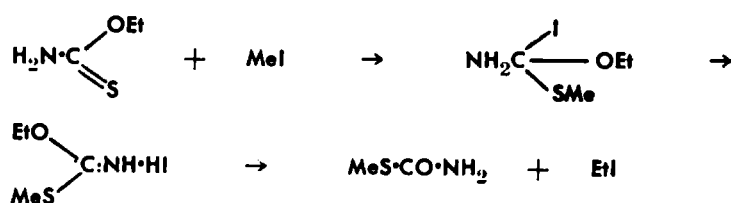


Quite a number of combinations of esters and alkyl halides were tried and in every case the alkyl in the $-\text{SR}$ group was the one

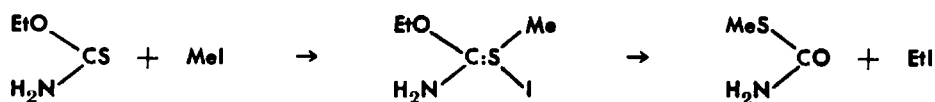
originally in the alkyl halide. A double ester resulted when ethylene bromide was the halide.^{1712a, 1712b} A similar reaction occurred when the acetylated thiourethan was kept at 40–45° with methyl iodide: ^{1714b}



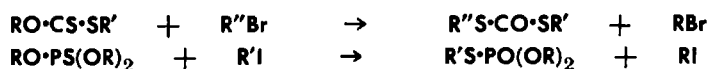
This reaction has been explained by assuming that the methyl iodide and the ester form a carbonium salt which then breaks up:



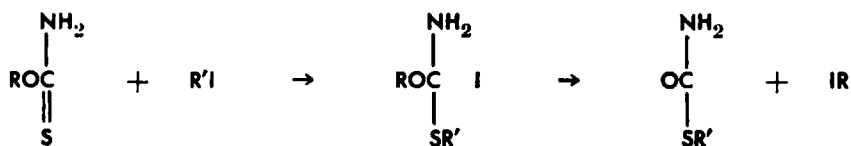
The salt $\text{EtO}(\text{MeS})\text{C}:\text{NH}\cdot\text{HI}$ melts at 58–60° and can be converted to the chloride by treatment with potassium carbonate, followed by hydrochloric acid.^{947a, 947b, 947c} It seems more reasonable to formulate it as the formation and decomposition of a sulfonium salt: ^{1713, 1714a}



It has been shown earlier that xanthogenic (chapter 2) and thiophosphoric esters (p. 300, Vol. I) undergo similar reactions:

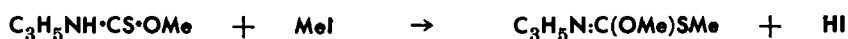


These were explained by assuming phosphonium intermediates. Another formulation has been given: ^{114d}

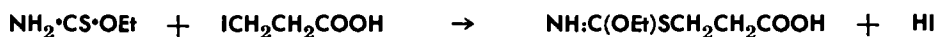


The reaction of Ph_2CHBr with ROCSNHR has been used for the preparation of complicated bromides.³³³ It is usually more difficult to disrupt an alkyl-sulfur bond than an alkyl-oxygen.

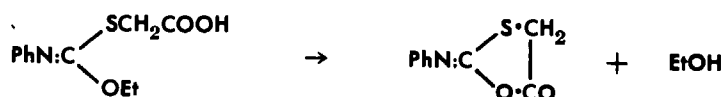
In the case of an N-alkyl urethane this reaction may take another course, hydriodic acid being eliminated rather than an alkyl iodide: ^{1019b, 1454}



This can be explained by assuming the same intermediate. The same reasoning applies to the reactions of alkyl halides with thioamides and with thiourea which will be considered in a later chapter. Esters of the type HN:C(OR)SR' are converted to guanidine hydrochloride by ammonium chloride but not by ammonia.^{947b} Xanthogenamide condenses with iodopropionic acid:



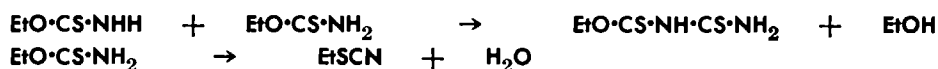
This goes on to a thiazine.⁹⁷⁹ Xanthogenanilide reacts similarly with chloracetic acid:



A molecule of ethanol is lost and a cyclic compound is formed.^{1019a}

Ethyl allylthiourethan forms a silver salt, $\text{EtO}\cdot\text{C}(:\text{NC}_3\text{H}_5)\text{-SAg}$ which may react with an alkyl halide.^{1452, 1454, 1457} The silver salt, $\text{CH}_2:\text{CHCH}_2\text{N:C(OEt)SAg}$, m. 170° , shows thermochromism. It is colorless at 0° , bright yellow at 15° , and lemon yellow at 30° , above which it does not change color. The methyl and propyl esters act similarly.¹⁴⁵⁶

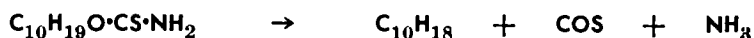
Phosphoric anhydride abstracts one molecule of alcohol from two of a thiourethan or a molecule of water from one:



The products are ethyl dithioallophanate and ethyl thiocyanate. Some rearrangement takes place:¹¹⁵



Menthyl thiourethan decomposes, on heating, to give menthene, just as menthyl methyl dithiocarbonate would do:



Ethyl thiourethan behaves quite differently:



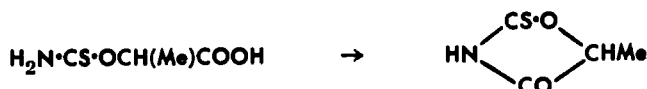
c-Hexyl thioncarbanilate heated to 240° at atmospheric pressure gives carbon oxysulfide, *c*-hexene, *c*-hexanol, and symmetrical diphenyl thiourea.³³³

The menthyl urethan is hydrolyzed by alkali:



Xanthogenamide is split by barium hydroxide into ethanol and thiocyanic acid.⁷⁵²

1-Thiocarbaminyl-lactic acid, m. 100–15°, $[\alpha]$ 20/D 16.6°, can be dehydrated to the cyclic 5-methyl-2-thion-4-oxo-oxazolidine, m. 114.5°, $[\alpha]$ 20/D –27.4°:⁷⁴⁷

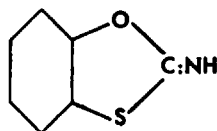


Xanthogenamide gives a red color with cupric chloride which is explained by assuming the intermediate formation of a complex before the final separation of the addition compound with cuprous chloride. Simultaneously there is formed as an oxidation product, a 1,3-thiadiazole which is formed also by oxidation with hydrogen peroxide.⁴⁷³ Xanthogenamide forms complex salts with cuprous chloride, bromide, and iodide¹³⁸³ and with salts of mercury, lead, cadmium, cobalt, nickel, iron, manganese, calcium,¹³⁸² and platinum.⁹⁸⁷

The thion esters show high molecular association, provided at least one amino hydrogen remains unsubstituted.²¹⁵

The therapeutic properties of thionurethans have been compared with those of urethan. The damage which they cause to the liver and kidney tissue contraindicates their use.⁴⁴⁵ A dilute solution of phenylthiourethan first stimulates and then paralyzes leech muscle. In large doses it is a vermifuge for puppies.⁸⁰⁰ Substituted thioncarbanilates, $\text{RC}_6\text{H}_4\text{NHCSOR}'$, in which R is alkyl or alkoxy show anthelmintic activity.^{303b, 1195} The butyl ester of *p*-allyloxythioncarbanilate combats mouse pinworms.¹³³³

Compounds of the type,



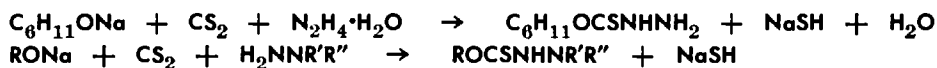
in which the benzene ring carries various substituents have been claimed as intermediates for dyes and pharmaceuticals.^{1708a} Di-

alkylaminourethans are said to be useful in pickling baths.^{1169b} Various thiourethans may be added to photographic developers or emulsions.^{20, 428} Salts of thiocarbamic acids have been used in plasticizing rubber or as vulcanization accelerators.^{669, 1628} Thioncarbamates have been recommended as pesticides¹⁵⁶⁵ and fungicides.^{132, 1514} They have also been proposed as flotation agents^{459a, 732a} and for improving the stability of acrylonitrile polymers.¹⁵⁴⁹

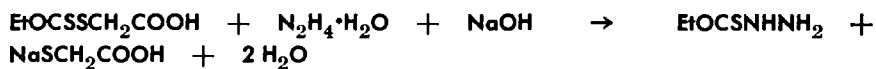
A complex cellulose thiourethan may form films or fibers.^{21, 22, 23, 1023b} Certain thiourethans are said to be useful in the vulcanization of rubber.^{331a} Thioncarbamates, ArOCSNR_2 , in which the aromatic group is a sulfonated phenol are useful in making fibers or insect repellants.¹⁵³⁹ Disubstituted thioncarbamates such as *i*-propyl diethylthioncarbamate, *i*- $\text{PROCSN}(\text{Et})_2$, are plant growth stimulants.¹⁵⁶⁵ Aminoalcohol esters of monoalkylthioncarbamic acids show pronounced local anesthetic activity.¹⁷⁵⁹

ESTERS OF THIONCARBAZIC ACID

These esters may be made by the reaction of carbon disulfide on sodium alcoholates and hydrazine or substituted hydrazines: ^{11, 1679}



Or they may be prepared by the action of alkali and hydrazine on a xanthate: ¹⁶⁷⁸



These react with aldehydes and ketones to form hydrazones.^{11, 1678, 1679} The compounds $\text{ROCSNHNR}'\text{R}''$ show tuberculostatic activity.¹¹ Monosubstituted esters, $\text{ROCSNHNHR}'$, retard fungus growth on citrus fruit.⁸⁴

Dithiocarbamic Acids

INTRODUCTION

There are three classes of carbamic acids:



Corresponding to these there are three classes of dithiocarbamic acids:



The free acids are unstable and can seldom be isolated, but their salts are well known and their esters are important.¹⁴⁴² Their esters are commonly called dithiourethans.

The constitution of the acids and their esters has been discussed and the conclusion reached that the acids and salts are to be represented by:



in which M is a univalent metal. That the two sulfurs are different in the esters is shown by the fact that only one of the sulfurs exchanges.⁹⁰⁴ On the basis of dipole moment and infrared studies it has been concluded that the structure of dithiocarbamic acids with amines varies with the polarity of the solvent.⁶⁹⁰ The structures of the dithioacids and dithioesters appear to be similar to those of the xanthates and dithiocarbonates. The free acids and their esters have the same optical properties.⁷¹⁸ Dithiocarbamic acids have been reviewed.^{267a}

DITHIOCARBAMIC ACID, $\text{H}_2\text{N}\cdot\text{CS}\cdot\text{SH}$

If alcohol is saturated with ammonia and carbon disulfide added, colorless crystals separate after a time.^{401b, 1789b}



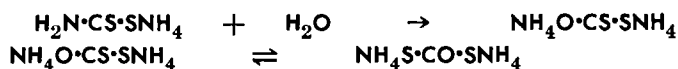
Ammonia and carbon disulfide may be brought together in various organic solvents.^{98, 1120a} They may be introduced continuously into the solvent and the ammonium dithiocarbamate withdrawn continuously.^{1120b} A somewhat modified synthesis has been given in Inorganic Syntheses III.¹¹¹⁹ An aqueous solution is formed where concentrated ammonium hydroxide stands in contact with carbon disulfide.¹²⁶⁸ Such a solution gives characteristic colored precipitates with many heavy metal ions and may be used in testing for them.^{693, 754, 1268} The dithiocarbamate method and its application to the determination of copper galenicals has been discussed.¹⁴⁶⁴

The importance of internal complex salts for analysis has been pointed out. Salt forming and complex forming groups must be present.^{470c} Thiocarbamic acid gives good tests for arsenic regardless of its valence.¹⁷⁰³

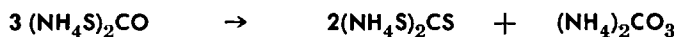
Guanidine and substituted guanidines with carbon disulfide form inner salts of the corresponding dithiocarbamic acids. These are useful for preparing cyclic nitrogen compounds.⁵⁸⁸ Biguanide gives a compound, $C_2H_5N_5CS_2$, which forms quite unstable salts.¹³²⁵

The addition of hydrochloric acid to a concentrated solution of the ammonium salt precipitates the unstable, crystalline, free acid, $H_2N \cdot CS \cdot SH$.^{1193a, 1194} It has also been obtained as an unstable oil.^{1789b} The value for K of this acid is 1.55×10^{-3} .⁷¹⁸ The free dithiocarbamic acid adds to unsaturated ketones, nitriles, or acids to form mercaptothiazines.^{850a}

On long standing in aqueous solution the ammonium salt is hydrolyzed:



The ammonium dithiocarbonate disproportionates into carbonate and trithiocarbonate: ^{1710b}



The lead, zinc, copper,^{401b} nickel, and cadmium⁹⁸ salts have been prepared by adding solutions containing the proper ions to a solution of this salt. The heavy metal salts, prepared in different ways, have been compared.⁴⁷¹ Ammonium dithiocarbamate reduces ferric chloride to the ferrous.¹⁴¹⁶ Iron and zinc salts of the acid reduce potassium ferricyanide and inhibit certain enzymes.¹²⁵⁹ The simple dithiocarbamates have been investigated spectroscopically.⁸⁹¹ Dithiocarbamates form complexes with molybdates which are useful in qualitative analysis. The unsubstituted carbamates are extracted more effectively from non-aqueous solvents than are the substituted.⁹⁶⁵

A rubber mix, not containing an accelerator, is dipped into a warm aqueous solution of a metal dithiocarbamate and then vulcanized.⁸²⁹ Esters and salts of thiocarbamic acids are vulcanized accelerators.^{225b, 225c} Dithiocarbamic acid derivatives stabilize the products of the reaction between rubber and sulfur

dioxide.⁶⁴⁶ Ammonium dithiocarbamate is effective in breaking the dormancy of potato tubers.¹¹⁵¹

Ammonium dithiocarbamate reacts with acetone, acetaldehyde, acrolein, and other aldehydes to give carbothialdines.^{1008b, 1193b} A dialkylammonium dithiocarbamate, $\text{H}_2\text{N}\cdot\text{CS}\cdot\text{SNH}_2\text{R}_2$, reacts with two molecules of an aldehyde: ^{1008a, 1008b}



MONOALKYLDITHIOCARBAMIC ACIDS, $\text{RNH}\cdot\text{CS}\cdot\text{SH}$

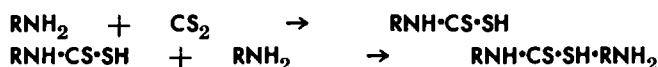
Preparation

The free monoalkyldithiocarbamic acids are unstable; however certain ones may be steam distilled.⁶⁰⁴

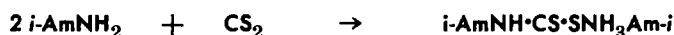
When two molecules of an amine react with one of carbon disulfide one of them goes into the anion and the other into the cation of the salt:



The reaction can be considered as involving two steps: the formation of a dithiocarbamic acid and the neutralization of this acid:



As the first step involves the transfer of a hydrogen atom from the amine to the sulfur, only ammonia and such amines as have a hydrogen attached to the nitrogen can undergo this reaction. Thus *i*-amyl amine and carbon disulfide brought together in dry ether form a crystalline compound:



This is the *i*-amylammonium salt of *i*-amyldithiocarbamic acid.^{778b, 779c, 780a, 1668} Methyl and ethyl amines react similarly.^{778b, 779c, 780a, 780b} This is a general reaction of primary amines.^{33, 171a} The reaction is so nearly complete that primary amines may be estimated by titrating the resulting dithiocarbamic acids with sodium hydroxide.³⁵⁵ A 45% solution of methylamine added to carbon disulfide, with cooling, gives a 96% yield of the salt, $\text{MeNH}\cdot\text{CS}\cdot\text{SNH}_3\text{Me}$.^{146b} Hexyl,⁵⁷⁵ pentadecyl,⁸⁵⁸ cetyl,¹⁶⁷¹ heptadecyl,¹⁶³⁷ *t*-butyl,^{168, 1399} oleyl, hydnocarpyl,¹⁶⁷¹ camphyl,⁶³⁸ fenchyl,¹⁶⁷⁶ and bornyl^{559, 1676} amines react satisfactorily. The

reactants may be brought together as vapors.^{432a, 1364} or in emulsion.^{816b, 830}

Ethylene diamine and carbon disulfide dissolve in alcohol to a clear solution which soon becomes turbid and deposits a white amorphous compound having the composition $(C_2H_4) \cdot H_4N_2CS_2$.^{781b} Treatment with alkali does not liberate ethylene diamine, which shows that one end of each molecule is in the anion. This would be the case if the product is a cyclic inner salt or a linear polymer:



2,3-Diaminobutane gives a similar polymer which loses hydrogen sulfide and forms symmetrical dimethylethylene thiourea, m. 198° .¹⁷⁸⁵ 2-Diethylaminoethylamine, $Et_2NCH_2CH_2NH_2$,¹³⁶¹ and 4-aminodiethylaminopentane, $Et_2NCH_2CH_2CH_2CH(NH_2) \cdot Me$,⁸⁸² give polymeric salts. Diamines where the amino groups are separated by 3 or more carbon atoms, form with carbon disulfide and sodium hydroxide, relatively unstable dithiocarbamates.^{404b, 1553} These dithiocarbamates give bis (β -cyanoethyl dithiocarbamates) on treatment with acrylonitrile.^{404b} 1,3-Diaminobutane,¹⁰⁸⁰ putrescene, and cadaverine¹⁵⁶⁹ give the dithiocarbamic acids: $H_2NCHMeCH_2CH_2NHCSSH$, $H_2NCH_2CH_2CH_2CH_2NH \cdot CS \cdot SH$, and $H_2NCH_2CH_2CH_2CH_2CH_2NH \cdot CS \cdot SH$, which appear to exist as inner salts. Heating an alcoholic suspension of the putrescene compound gives tetramethylene thiourea, m. 177° .¹⁵⁶⁹ Dithiocarbamic acids derived from aliphatic diamines, where the amine groups are separated by at least 6 carbon atoms and where at least one hydrogen is linked to nitrogen, form long chain polymers on heating.^{820, 1553} These polymers are used in foils, fibers, cements, adhesives, etc.⁸²⁰ The compound from hexamethylene diamine loses hydrogen sulfide when heated to 200° in a current of nitrogen. The thiourea that is left is polymeric and can be spun into long fibers:¹²⁴¹



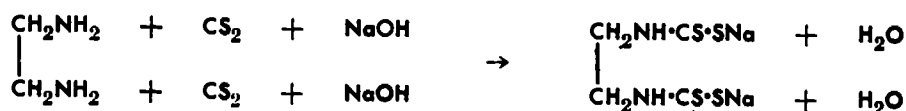
When a solution of the acid, $H_2N(CH_2)_3O(CH_2)_4O(CH_2)_3NH \cdot CS \cdot SH$, in 25% sodium hydroxide is boiled, an insoluble film forming condensation product is deposited.⁹¹⁵ From 1,4-diaminocyclohexane the dithiocarbamic acid, $H_2NCH(CH_2CH_2)_2CHNH \cdot CS \cdot SH$, has been prepared and tested as a Nylon inter-

mediate.⁸⁰⁴ Analogous compounds are formed from *cis*- and *trans*-1,2-diaminocyclobutane.²⁰⁸ Leucauramine with carbon disulfide gives the salt of the dithiocarbamic acid.¹¹⁶⁶ Alkylammonium dithiocarbamates are recommended as antioxidants for medicinal oils.⁵²⁶

When an aliphatic amine is added to a suspension of carbon disulfide in ammonium hydroxide, the ammonium salt of the monosubstituted dithiocarbamic acid is formed.^{81, 1446, 1780} When it comes to forming other salts of the dithiocarbamic acid, a strong base, inorganic or organic, will serve. One molecule of the amine and one of an alkali react with carbon disulfide:^{887b, 888}



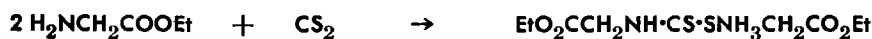
The amine is dissolved in three or four parts of water, the calculated quantity of carbon disulfide is added slowly with stirring and then sodium hydroxide.^{409a, 413b} The other reactants can be mixed and the carbon disulfide added last. Amyl and diamyl amines and sodium or potassium hydroxides react with carbon disulfide.¹²⁴⁷ From ethylene diamine the sodium salt of ethylenebis-thiocarbamic acid is obtained:¹⁷⁶⁸



The result here is quite different from the polymeric product which is obtained when one molecule of the diamine reacts with one of carbon disulfide. Aeration of a water solution of this salt gives a variety of products including thiurams and thioureas.^{1058, 1610}

Spermine reacts with $\text{MeS}\cdot\text{C}(\text{:NH})\text{NH}_2\cdot\text{HI}$ liberating methyl mercaptan and forming a diguanide dihydroiodide. The free base from this unites with carbon disulfide to form spermine-diguanidedithiocarbamic acid, m. $160-5^\circ$.¹⁷⁶³

Ethyl aminoacetate reacts with carbon disulfide:^{544a, 872, 874a}

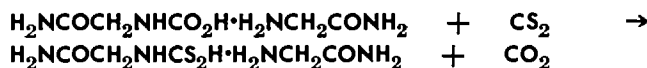


From this the silver and mercury salts $\text{EtO}_2\text{CCH}_2\text{NH}\cdot\text{CS}\cdot\text{SAg}$ and $(\text{EtO}_2\text{CCH}_2\text{NH}\cdot\text{CS}\cdot\text{S})_2\text{Hg}$, have been prepared. Oxidation with iodine gives $\text{EtO}_2\text{CCH}_2\text{NH}\cdot\text{CS}\cdot\text{S}\cdot\text{S}\cdot\text{CS}\cdot\text{NHCH}_2\text{CO}_2\text{Et}$.

Aminoacetic acid, ammonia, and carbon disulfide give the diammonium salt:



Potassium ⁹⁵¹ or barium hydroxide ^{1049a} may be used in place of the ammonia. From glycylglycine the salt, $\text{NH}_4\text{O}_2\text{CCH}_2\text{NH}\cdot\text{COCH}_2\text{NH}\cdot\text{CS}\cdot\text{SNH}_4$, has been prepared. Alanine reacts regularly.^{27c} The reaction of glycine and alanine with carbon disulfide has been investigated polarographically and can be used for the determination of these amino acids.¹⁷⁸⁷ With potassium hydroxide instead of ammonia, the potassium salt, $\text{KO}_2\text{CCH}_2\text{NH}\cdot\text{CS}\cdot\text{SK}$, is obtained.⁶⁷⁶ Phenylglycocoll, sarcosine, and asparagine yield the expected compounds but some of the other amino acids do not.¹⁴⁹⁸ An alkaline solution of a protein is said to react with carbon disulfide.¹⁶⁴⁶ A method for the controlled degradation of peptides using carbon disulfide has been proposed.⁹⁹⁹ Carbamyl-carboxylic acids are converted to the dithio compounds: ⁷⁸⁴



N-Thiocarbamylsuccinamic acid serves as an accelerator in the vulcanization of rubber.¹⁷⁹³

A study has been made of the kinetics of the decomposition of the dithiocarbamylcarboxylic acids in acid medium to the corresponding amino acid and carbon disulfide. This decomposition is a reversal of the formation of these compounds.¹⁷⁸⁶

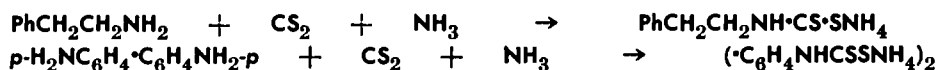
Aniline being a weak base requires the help of ammonia: ^{582, 913, 1049a}



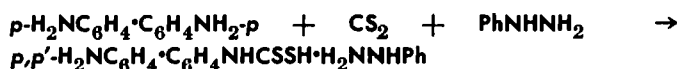
A mixture of 93 g. aniline, 76 g. carbon disulfide, and 300 cc. concentrated aqueous ammonia, standing twelve hours, gives 130 g. or 70% yield of the salt.⁵⁸² The potassium salt, $\text{PhNH}\cdot\text{CS}\cdot\text{SK}$, and the barium salt, $(\text{PhNH}\cdot\text{CS}\cdot\text{S})_2\text{Ba}$, result when the hydroxides of these metals are substituted for the ammonia.^{1049a}

This reaction can be used for taking carbon disulfide out of gases, such as illuminating gas. The gas is passed over a mixture of an amine and a metal oxide. The thiocarbamate salt that is formed may be decomposed to regenerate the amine for reuse.^{612, 1130, 1131} A ready formed amine dithiocarbamate may be used along with a metal oxide.¹³⁷³

Other aromatic amines react with ammonia: 209, 746, 1049b



Phenyl hydrazine may be substituted for the ammonia. With benzidine only one amino group reacts: 1049b



Aniline, carbon disulfide, and potassium hydroxide react: 1332a



This salt can be made in another way by boiling the xanthate with aniline: 1332a, 1535



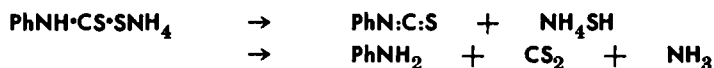
With aniline, potassium carbonate also serves as the alkali.⁷⁶¹

Heterocyclic amines form dithiocarbamic acids. A tertiary alkyl amine may replace the ammonia in this reaction: 368, 732b



These are useful as pesticides^{732b} and fungicides.³⁶⁸

The ammonium salt of dithiocarbanilic acid decomposes in two ways:



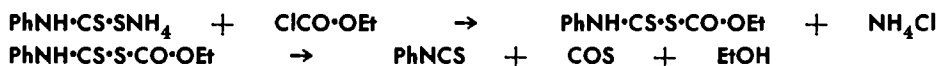
The formation of a mustard oil is favored by the presence of heavy metal salts. To prepare phenyl isothiocyanate, add a solution of copper sulfate to the ammonium salt and distill with steam. The yield is quantitative.^{1049a} As this is a much used method of making mustard oils, it is discussed more fully in the thiocyanate chapter in Volume V, to which reference should be made. Hofmann used silver nitrate and mercuric chloride.^{778c, 780c} Weith used ferric chloride.¹⁶⁹⁸

Ammonium dithiocarbanilate is a reagent for copper ions.¹⁶¹² It forms a nickel salt, $\text{Ni}(\text{SCSNHPh})_2$, which forms a complex compound with sodium polysulfide, $\text{Na}_2[\text{S}_2\text{Ni}(\text{SCSNHPh})_2]$.⁷⁶¹

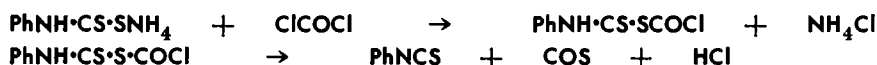
Aminocamphor and carbon disulfide give the acid $\text{C}_8\text{H}_{14}(\text{CO})\text{-CHNH}\cdot\text{CS}\cdot\text{SH}$, m. 128°. At 170° the methyl ester is split into methyl mercaptan and camphoryl mustard oil.^{507, 560} Trimethyl-

silylmethyl amine forms a dithiocarbamic acid whose lead salt decomposes on heating to form the isothiocyanate, $\text{Me}_3\text{SiCH}_2\text{-NCS}$.¹²³³

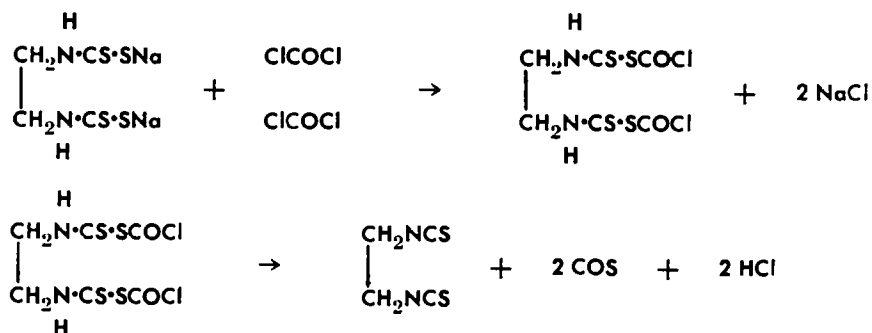
The reaction of ammonium phenyldithiocarbamate with ethyl chloroformate is the first step in the formation of a mustard oil.^{27a}



Methyl amine undergoes the same reaction.⁸⁸⁸ The reaction with phosgene may be represented as following a similar course:^{1350, 1523}



The reaction with chlorine gives mustard oil, aniline, and ammonium chloride.¹⁰⁹⁵ Ethylene diisothiocyanate is similarly obtained from ethylene bisdithiocarbamic acid:



The decomposition of the dichloroformyl derivative takes place when it is heated to 59° in a vacuum.¹⁷⁶⁸ Aromatic isothiocyanates have been prepared from an aromatic dithiocarbamate coupled with a salt of an α -halocarboxylic acid.⁹¹³ This has been patented.¹²¹⁸

The reaction of acrylonitrile with benzyl dithiocarbamic acid has been studied under various conditions. In aqueous solution benzyl isothiocyanate and $\text{S}(\text{CH}_2\text{CH}_2\text{CN})_2$ are the chief products; in the presence of benzyl amine and acetic acid, $\text{PhCH}_2\text{-NHCS}_2\text{CH}_2\text{CH}_2\text{CN}$ is the chief product.^{404c}

The potassium salt decomposes on heating:



Under some conditions the potassium sulfide and carbon disulfide may unite: ¹²³⁵



The ammonium salt of the dithiocarbamic acid from α - or β -naphthyl amine gives the same results.⁷⁴⁶ Heating an alkylammonium alkyldithiocarbamate in alcohol solution is a way to prepare symmetrical dialkylthioureas: ^{780b, 1301b}



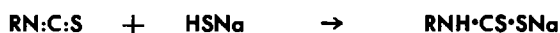
A dialkylammonium salt, which may be obtained from a monobasic diamine by double decomposition, gives a trialkylthiourea: ^{821, 1707b}



It would seem that a tetraalkylthiourea should result from a dialkylammonium dialkyldithiocarbamate, $\text{R}_2\text{N}\cdot\text{CS}\cdot\text{SNH}_2\text{R}_2$, but such is not the case.^{1707b} As these are accepted methods of preparing thioureas they are more fully treated in the chapter on thiourea.

Concentrated sulfuric acid and aliphatic or alicyclic thiocyanates at 0° form thiocarbamates. Numerous simple and polymethylene thiocarbamates were prepared in this way.^{1358b}

A sodium dithiocarbamate results when sodium hydrosulfide is added to a mustard oil:



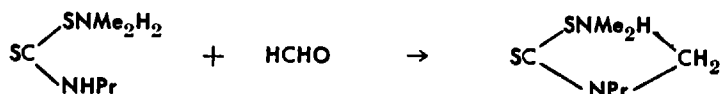
The industrial preparation of dithiocarbamates has been described.⁵⁴

The alkali, alkaline earth, lead, and zinc salts of the dithiocarbamic acids are colorless, but the copper, nickel, cobalt, and iron salts are highly colored and may be used in chemical analysis. They may be internal complexes.^{409b, 413c} A large number of these salts have been prepared, particularly sodium, nickel, cobalt, and copper salts of the acids, $\text{MeNH}\cdot\text{CS}\cdot\text{SH}$, $\text{EtNH}\cdot\text{CS}\cdot\text{SH}$, $\text{PrNH}\cdot\text{CS}\cdot\text{SH}$, $\text{Me}_2\text{N}\cdot\text{CS}\cdot\text{SH}$, $\text{Et}_2\text{N}\cdot\text{CS}\cdot\text{SH}$, and $\text{Pr}_2\text{N}\cdot\text{CS}\cdot\text{SH}$.^{323b}

Arsenic salts, $(\text{RNH}\cdot\text{CS}\cdot\text{S})_3\text{As}$ are precipitated as thick oils when hydrochloric acid is added to a solution containing a sodium salt, $\text{RNH}\cdot\text{CS}\cdot\text{SNa}$, and sodium arsenite.^{1092c}

Methylammonium methyl dithiocarbamate reacts with two

molecules of an aldehyde. The product was originally thought to be a carbothialdine, but spectroscopic evidence favors a substituted 1,3,5-thiadiazine.^{8, 146b} Only one molecule of formaldehyde reacts with dimethylammonium propyldithiocarbamate:^{1007c}



Ethanolamine and carbon disulfide unite to form the dithio acid, $\text{HOCH}_2\text{CH}_2\text{NH}\cdot\text{CS}\cdot\text{SH}$. On standing this loses a molecule of water to go into 2-mercapto-oxazoline.¹⁴⁸³ But if the original reactants are heated together under pressure the water is eliminated in a different way and the product is 2-mercaptothiazoline, which is said to be an excellent accelerator.^{485, 1103}

2,3-Dihydroxypropyl amine reacts with carbon disulfide to give an intermediate which condenses similarly to 2-mercapto-5-hydroxymethylloxazoline. The reactions with glucamine follow the same course ending up with a 2-mercapto-oxazoline having the group $\text{—CH(OH)CH(OH)CH(OH)CH}_2\text{OH}$ in the 5-position.¹³⁹⁴ Other amines containing several hydroxyl groups react in a similar manner.^{1103, 1394, 1395}

Derivatives of dithiocarbamic acid vary in their reactivity according to their structure. When there is only one substituent on the nitrogen, they can be determined bromometrically or with iodine in alkaline solution. They can also be determined gravimetrically by oxidation with nitric acid or hydrogen peroxide and precipitation of the sulfate ion as barium sulfate. If the nitrogen is tertiary they are more difficult to oxidise and 30% hydrogen peroxide and 10% sodium hydroxide must be used.¹⁷⁵⁶ Salts of ethylene bisdithiocarbamic acid are analyzed by decomposing in acid medium and absorbing the carbon disulfide in alcoholic potassium hydroxide and titrating the xanthate with iodine.^{558, 1389}

Uses

The uses of dithiocarbamates in organic synthesis and their applications in emulsion polymerization have been outlined.³⁷⁶

There has been considerable interest in the disodium salt of ethylene bis-dithiocarbamic acid, $(\text{NaSCSNHCH}_2)_2$, called Dithane, as a fungicide and pesticide.^{83, 170, 380, 446, 447b, 585, 634b, 757a,}

758a, 759, 838, 859, 890, 945, 992a, 1013, 1030, 1059, 1087, 1152, 1187, 1199, 1341, 1378, 1466, 1502, 1517, 1518, 1534, 1580, 1731b, 1747, 1754 The zinc salt has received much attention.^{142, 169, 224, 334, 379, 380, 392, 537, 563, 838, 859, 890, 977, 983, 1030, 1086, 1087, 1127, 1285, 1345, 1379, 1534, 1595, 1604, 1754, 1755, 1802} Its preparation⁶⁹⁸ and stabilization^{869, 1060} have been patented. One patent suggests that shipping the diammonium salt is cheaper and that addition of zinc sulfate will give two purpose spray—fungicidal and fertilizing.⁵³⁷ The composition of a dust containing this salt has been patented.³³⁷ There is evidence of synergism between the zinc salt and copper containing fungicides in the control of vine mildew.¹²⁷⁵ It reduces downy mildew on spinach, beets, and lettuce by 98%.¹⁷⁷³ The ferric, cupric,^{757a} manganous,^{551, 636, 797, 1086} as well as related compounds^{189, 633, 911, 1286} have been claimed as fungicides and described in detail. Their safe use has been studied.^{30, 890} Sodium methyldithiocarbamate was very effective as a fungicide in a special method of application.¹⁷⁹²

Zinc and other dithiocarbamates have been of interest in the vulcanization of rubber.^{879b, 1214} Salts of the bis-dithiocarbamic acid, $(\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}\cdot\text{CS}\cdot\text{SH})_2$, from hexamethylene diamine are recommended as vulcanization accelerators and insecticides.^{1736b} The reaction product of formaldehyde with an ammonium salt of an aryldithiocarbamic acid is claimed as an insecticide or fungicide.⁷ The condensation product of an aldehyde, with at least two carbon atoms, an aliphatic or aromatic primary amine, and carbon disulfide is claimed as an accelerator.^{483a} Cyclohexylamine reacts with an aldehyde and then with carbon disulfide to produce a vulcanization accelerator.^{1169a, 1495a}

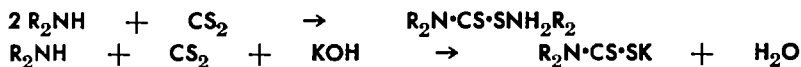
The metal salt of a substituted dithiocarbamic acid is useful in hydraulic transmission fluids.¹⁵⁵ The primary swelling of gel fibers from viscose is reduced by the addition of certain N-substituted dithiocarbamic acids.⁴⁴⁴ The dithiocarbamate from a halogenated β -alkenylamine is recommended as a polymerization regulator.⁷³

DIALKYLDITHIOCARBAMIC ACIDS, $\text{R}_2\text{N}\cdot\text{CS}\cdot\text{SH}$

Preparation

The reaction of secondary amines with carbon disulfide has been exploited extensively since many commercially useful com-

pounds are among the products. Two molecules of the amine ¹⁹³, 408a, 408b, 412c, 716, 815, 1566 or one of the amine and one of alkali ^{727c}, 952, 1092a, 1092c, 1092d, 1093c, 1588 may be used:



Emulsifying agents may facilitate the reaction.^{816b, 816c, 830, 1694} The dimethyl ammonium salt of dimethyldithiocarbamic acid may be prepared by the action of dimethylamine on tetramethylthiuram sulfide in benzene at 100°.^{410c} The diethylammonium salt of diethyldithiocarbamic acid, containing S ³⁵ has been prepared from carbon disulfide with two atoms of this isotope.⁵⁰⁰ A study has been made of the kinetics of the sulfur exchange in NaS₂CNEt₂ with radioactive sulfur under various conditions.^{688, 691, 963}

The sodium derivative of a diaryl amine combines with carbon disulfide: ^{644a, 1481}



The required sodium derivative may come from sodamide and the amine.^{878a} Dimethylformamide, HCONMe₂, can take the place of dimethylamine in its reaction with carbon disulfide and alkali.⁷⁶³

Heavy metal salts of dialkyldithiocarbamic acids are obtained by adding a dialkyl amine and carbon disulfide to an ammoniacal solution of a heavy metal salt.⁸²⁸ Instead of a metal hydroxide, a heavy metal salt of a weak acid may serve in preparing dialkyldithiocarbamates. Thus ethylaniline, carbon disulfide, and zinc acetate give the zinc salt (PhEtN·CS·S)₂Zn.³⁵⁰ Boiling ethylaniline, carbon disulfide, and zinc hydroxide in alcohol gives the same salt.⁹⁷² Or metallic oxides, such as those of zinc, barium, lead, or copper, bring about the reaction.^{1248b} Instead of the alkali, freshly precipitated and partially dried ferric hydroxide has been used with carbon disulfide and the amine to prepare ferric dibutyl-, dipropyl-, di-*i*-propyl-, and propyl-*i*-propyldithiocarbamates, (R₂N·CS·S)₃Fe.²³⁸

Ferric salts of improved stability can be made by adding water soluble ferric salts in less than chemically equivalent amounts to water solutions of dialiphatic dithiocarbamates.^{1170b}

The nitroso salts, (Me₂N·CS·S)₂FeNO and (C₅H₁₀N·CS·S)₂-

FeNO, have been made starting with (NOFe)SO₄. There are analogous cobalt salts, (R₂N·CS·S)₂CoNO.^{234a} Passing nitric oxide into a solution of chromous acetate and sodium diethyldithiocarbamate gives dinitrosylchromic diethyldithiocarbamate, (ON)₂Cr·CS·NEt₂.^{1093a} The corresponding extremely unstable vanadous salts, (ON)V[SCSNR₂]₂, are diamagnetic.^{1093b} The vanadium salt of diethyldithiocarbamic acid is quantitatively extracted from acid solution by ethyl acetate or chloroform.²⁸⁴

The reaction of di- or mono-alkylated dithiocarbamates with aluminum salts yields a precipitate of a basic salt. With gallium salts easily hydrolyzable and with indium salts relatively stable dithiocarbamates are obtained.^{415c}

To prepare arsenic dimethyldithiocarbamate three molecules each of dimethylamine, carbon disulfide, and sodium ethylate in alcohol are mixed and one molecule of arsenic trichloride is added at -15°. The salt (Me₂N·CS·S)₃As decomposes without melting. The diethyl, dipropyl, dibutyl, and di-*i*-butyl salts have been obtained by double decomposition from arsenic trichloride and the corresponding sodium salts.^{1092c} Ruthenium, rhodium, and palladous dialkyldithiocarbamates have been prepared. The chromic salts, (R₂N·CS·S)₃Cr, are stable in air and in organic solvents. They have an intense violet blue color.^{1092a}

The preparation of a salt KUC₁₅H₃₂O₃S₃ has been reported. Spectroscopic evidence indicates that this is the salt of the tetrakis(diethyldithiocarbamate)-uranate ion.¹⁸⁰¹ Ammonium uranyldithiocarbamates, [H₂NRR'] [UO₂(S₂CNRR')₃], have been prepared and their melting points determined.¹²

Complex salts of polonium with dialkyldithiocarbamates of cobalt, bismuth, copper, and nickel have been prepared in which polonium has the valence three and coordinate number six.⁶⁸⁵ Diphenylamine and titanium tetrachloride in carbon disulfide give the compound (Ph₂N·CS·S)₄Ti.⁴²⁷

Ethyl methylaminoacetate has been the starting point for making a mercury salt, (EtO₂CCH₂NMe·CS·S)₂Hg. Saponification results in the unstable sodium salt, (NaO₂CCH₂NMe·CS·S)₂Hg.⁵⁶⁵ There are others with different alkyls on the nitrogen.¹⁰⁰⁰ The synthesis of the dithiocarbamates and xanthates of selenium II and tellurium II has been described in *Inorganic Syntheses*.^{561c} Some of these salts are thermochromic.^{561b}

The compound from a diamine and carbon disulfide is con-

veniently written as the free acid, $\text{Et}_2\text{N}(\text{CH}_2)_n\text{NR}\cdot\text{CS}\cdot\text{SH}$, but is a cyclic inner salt or a polymer. This reacts with a dry heavy metal chloride to give a water-soluble amine hydrochloride, such as $\text{Et}_2\text{N}(\text{CH}_2)_n\text{NR}\cdot\text{CS}\cdot\text{SAg}\cdot\text{HCl}$. Alkali sets free the base, $\text{Et}_2\text{N}(\text{CH}_2)_n\text{NR}\cdot\text{CS}\cdot\text{SAg}$, which still contains the metal.¹⁴⁴³

Ammoniacal formaldehyde and carbon disulfide form the salt: $(\text{CH}_2\text{:N}\cdot\text{CS}\cdot\text{SNH}_4)_3$, from which mercury, cobalt, zinc, nickel, and silver salts have been made.^{1008a}

A large number of salts of iron, arsenic, zinc, nickel, cadmium, cobalt, copper, silver, and other metals have been made by double decomposition with the sodium and potassium salts from various dialkyl amines.^{1570, 1723} Many of the heavy metal salts have melting points, some of which are in the lists of physical properties. Copper salts can be prepared by shaking the corresponding thiuram disulfide with copper bronze in carbon disulfide or chloroform.^{9, 571c} Sodium dimethyldithiocarbamate and cadmium chloride under conditions of turbulent flow give a quantitative yield of the salt.^{484c} Cadmium ion and sodium diethyldithiocarbamate give the cadmium salt, soluble in organic solvents.²⁸⁴ A process has been described for the preparation of manganese dimethyldithiocarbamate.¹⁶⁶

Cyanosubstituted secondary amines form dithiocarbamic acids which precipitate heavy metal salts.^{727c}

Trimethylamine combines with carbon disulfide to give $\text{Me}_3\text{N}\cdot\text{CS}_2$, m. 125° . This forms compounds with acids and with mercuric chloride.¹³⁴ The tertiary amine does not react at 25° .¹⁹³ Trimethylphosphine forms a 1:1 addition compound with carbon disulfide.¹⁹³ Triethylphosphine unites with carbon disulfide but the constitution of the product is not known.^{719, 778a, 779b} This with the addition of methyl iodide forms a salt, $\text{Et}_3\text{PCS}_2\text{MeI}$, which is probably a phosphonium iodide.^{861a}

Dithiocarbamates from Cyclic Amines

An important group of dithiocarbamates is that in which the secondary amine is cyclic. The most available amine of this class is piperidine. Its derivatives have been extensively studied. It reacts readily with carbon disulfide to give the salt $(\text{CH}_2)_5\text{N}\cdot\text{CS}\cdot\text{SN}(\text{CH}_2)_5\text{H}_2$, piperidinium pentamethylenedithiocarbamate or pentamethyleneammonium pentamethylenedithiocarbamate.^{203, 943, 1302, 1719} The silver, bismuth, copper, cobalt, lead, and manga-

nese salts have been studied.⁴⁷² They are extremely insoluble. The manganese salt is oxidised rapidly in the air, as are the manganese salts of the corresponding dithiocarbamic acids derived from di-*i*-butyl and dibenzyl amines.^{234b} Aminotrimethylpiperidine unites with carbon disulfide. The product, $\text{H}_2\text{NC}_3\text{H}_{16}\text{NH}\cdot\text{CS}\cdot\text{SH}$, is written as the free acid, but it is to be regarded as an inner salt.⁷³⁰

In ether solution trimethyleneimine and carbon disulfide form the salt $(\text{CH}_2)_3\text{N}\cdot\text{CS}\cdot\text{SH}_2\text{N}:(\text{CH}_2)_3$.⁸⁰⁶ The cyclic ethyleneimine forms the salt $(\text{CH}_2)_2\text{N}\cdot\text{CS}\cdot\text{SH}_2\text{N}:(\text{CH}_2)_2$.^{818c} Ethyleneimine and carbon disulfide are used in making a synthetic resin which may contain dithiocarbamic units. The reaction may be carried out in various ways.^{509, 817d, 819} Other cyclic amines react similarly, $(\text{CH}_2)_6\text{N}\cdot\text{CS}\cdot\text{SN}(\text{CH}_2)_6\text{H}_2$.^{1215a} Carbon disulfide unites with formaldehyde-ethyleneimine, $(\text{CH}_2:\text{N}(\text{CH}_2)_2)_n$, to give $\text{CS}_2((\text{CH}_2)_2\text{N}:\text{CH}_2)_2$, m. 75° .^{407b}

Piperazine and carbon disulfide form the acid $\text{HN}(\text{CH}_2\text{CH}_2)_2\text{N}\cdot\text{CS}\cdot\text{SH}$, which is soluble in alkali but is decomposed by acids.²⁷³ This reaction can be used to advantage in the detection of carbon disulfide.^{258a} Imidazolyl dithiocarbamic acids have been similarly prepared. These compounds have been separated by paper ionophoresis.¹⁷⁸⁸ Compounds such as $(+)\text{H}_3\text{NCH}_2\text{CH}_2(\text{C}_8\text{H}_{17})\text{NCS}_2(-)$ have been prepared from $\text{C}_8\text{H}_{17}\text{NH}(\text{CH}_2)_2\text{NH}_2$ and carbon disulfide. These inner salts give 1-alkyl-2-imidazolidine-thiones on heating or on treatment with carbon disulfide.¹⁰³⁷

N,N' -di-*c*-hexyl ethylene diamine forms a monodithiocarbamic acid which on heating loses hydrogen sulfide to give 1,3-di-*c*-hexyl-imidazolidinethione-2.¹⁷⁹⁷ Morpholine, carbon disulfide, and alkali react.^{363, 597}

Reactions

Salts of disubstituted dithiocarbamic acids decompose: ^{1129a}

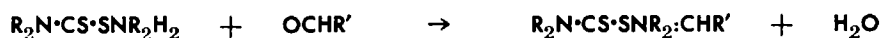


The formation of a thiourea by the action of an amine on a dithiocarbamic salt has been claimed: ¹⁴⁴⁰



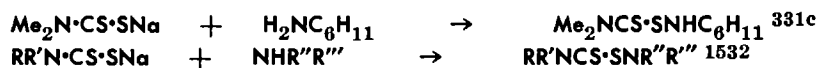
Zinc dimethyldithiocarbamate forms complexes with amines.^{79, 1075a}

Aldehydes react with dialkylammonium dialkyldithiocarbamates: ^{1006a}



The similar reactions which take place with monoalkyl and unsubstituted dithiocarbamates have been mentioned earlier in this chapter. Salts of dithiocarbamic acid react with chloramine, $CINH_2$ ^{1648c} with cyanuric chloride, ^{825, 1255} or with N-chlorosuccinimide ¹⁶⁸⁷ to make vulcanization accelerators.

Oxidative condensation of the sodium salt of a dialkyl dithiocarbamic acid and a primary or secondary amine yields a thiocarbamyl sulfenamide:



These are also accelerators. ^{331c} A mixed disulfide or alkyl sulfenedithiocarbamate, $RR'N \cdot CS \cdot SSR''$, is obtained by treating a dialkyldithiocarbamate, $RR'N \cdot CS \cdot SNa$, and a mercaptan, $R''SH$, with thiocyanogen. ^{812b} Benzothiazolyl disulfide reacts with the salt to give the same type of compound. ^{723c} These are said to be powerful accelerators for the vulcanization of rubber. ¹⁵⁷⁸

A salt of an N-substituted dithiocarbamic acid reacts with an alkyl thiosulfenyl halide in inert organic solvents to give alkylthiosulfenyl dithiocarbamates, $RSS \cdot S \cdot CSNR'R''$. ^{766b} An S-acyl derivative, such as $Me_2N \cdot CS \cdot SCOPh$, a mixed anhydride rather than an ester, is a secondary accelerator. ^{1215b}

Properties

Properties of specific compounds appear in the tables at the end of the chapter.

Diethyldithiocarbamic acid is stable at pH 1–3. ^{1113a} Carbon disulfide and diethylamine in alcohol show an anodic wave due to formation of the salt. This can be used for analytical purposes. ^{1805a} At pH 7–12 the sodium salt of this acid gives an abnormally small anodic wave. Polarograms indicate dissociation constant is at least 10^{-7} . ¹⁴¹⁹ The polarographic behavior of the acid can be interpreted as a reaction with Hg_2^{++} and subsequent formation of a monomeric soluble mercury salt. ²³² The composition, structure, and analytical application of the mercuric salt, $Hg(SCSNEt_2)_2$, have been examined. ^{144a}

The solubilities in organic solvents of metal diethyldithiocarbamates increase in this order: thallium, arsenic, zinc, ferric, nickel, cadmium, lead, cobalt, copper, silver, and mercury.^{1093c} The solubility of zinc dimethyl dithiocarbamate in benzene and toluene in the presence of an organic base has been attributed to complex compounds formed with the free electron pair of the nitrogen atom in the base.¹⁶³⁵

The primary and secondary stability constants of several copper dialkyldithiocarbamates have been determined in 75% ethanol-water solutions.⁸⁵² The stabilities and magnetic properties of a number of ferric, nickel, and copper salts, $(R_2N\cdot CS\cdot S)_3\text{-Fe}$,²³⁶ $(R_2N\cdot CS\cdot S)_2\text{Ni}$,²³⁵ $(R_2N\cdot CS\cdot S)_2\text{Cu}$, and $(R_2N\cdot CS\cdot S)\text{Cu}$ ^{233, 235} have been investigated, so have the polymorphism and magnetism of the nickel and copper dipropyl, dibutyl, di-*i*-butyl, and di-*i*-amyl dithiocarbamates.¹⁰⁹⁴ The planar configuration and diamagnetism of the nickel dipropyl- and dibutyldithiocarbamates have been studied.²⁶² The crystal structures of nickel and copper dipropyldithiocarbamates have been determined.¹²⁸² Zinc diethyldithiocarbamate is monoclinic with four molecules per unit cell.¹⁵¹⁰ The electric moments of the dialkyldithiocarbamates are in accord with those to be expected of a symmetrical chelate arrangement of the radicals around the metals.^{1092c, 1092d} The parachor values of diethylammonium diethyldithiocarbamate have been measured and found to disagree with the calculated values. The negative anomaly is attributed to resonance effects, H-bonds, and polar effects in the proposed structures.^{149, 150}

The infrared spectra and structure of a representative group of N,N-dialkyldithiocarbamates and their derivatives were investigated.^{275b}

Physiological

Potassium diethyldithiocarbamate is toxic to rats.⁸⁶⁰ The zinc and copper salts of the dimethyl acid in the diet for two years did not affect growth or mortality of rats.⁷⁷⁶ The dimethylammonium salt of the same acid and diethylammonium diethyldithiocarbamate are not toxic to silk worms.^{627, 628} The sodium salt of the dimethyl acid has low toxicity and kills spirochetes in dilutions of one in two million.^{468b} The potassium salts of the monomethyl- and diethyldithiocarbamic acids had bacteriostatic effect in the presence of serum.⁸⁶⁰ The sodium diethyl-, dibutyl-,

and di-*i*-amylthiocarbamate and the dibenzylammonium salt of dibenzylthiocarbamic acid are ineffective as bactericides but highly bacteriostatic on both gram positive and gram negative bacteria.¹¹⁸¹ Certain dialkylthiocarbamic acid salts are used in detergents because of their antibacterial activity.¹⁰³⁵ Zinc dimethylthiocarbamate has been tested as a skin disinfectant in soap.¹³²²

The mode of action of sodium dimethylthiocarbamate on *Aspergillus niger* has been examined.¹⁵⁰⁰ The effects of sodium diethylthiocarbamate on various strains of *B. suis* and *B. melitensis* have been tried.³⁷⁰ The toxic influence of copper could be reversed or prevented by diethylthiocarbamate in growth and glucose metabolism in fluid cultures of *Escherichia coli*.¹⁴¹¹

The sodium salts, $\text{EtNH}\cdot\text{CS}\cdot\text{SNa}$, $\text{Et}_2\text{N}\cdot\text{CS}\cdot\text{SNa}$ and $\text{PrNH}\cdot\text{CS}\cdot\text{SNa}$, produce an increase in blood glucose in young rabbits.^{246a} Diethylammonium diethylthiocarbamate is therapeutically useful in several ways.¹⁰⁷⁸ Sodium diethylthiocarbamate and piperidinium and sodium pentamethylenedithiocarbamate were toxic to sarcoma cells and embryonic mouse fibrocytes.¹³⁰⁸ Diethylammonium salt of diethylthiocarbamic acid protects against immediate x-ray radiation (Co^{60} source) and inhibits post-irradiation effects on polystyrene.⁵⁶⁶ Diethylthiocarbamate greatly decreases or prevents the effects of α,β - and β,γ -angelica lactones on the heart.¹¹³⁵ It inhibits the anerobic oxidation of vitamin C in the press juices of various vegetables.¹⁵⁰⁶ The sodium salt prevented destruction of vitamin B_{12} by copper, molybdenum, and others in the presence of ascorbic acid.¹⁵⁵⁰ The salts of diethylthiocarbamic acid poison enzyme preparations for the oxidation of ascorbic acid by copper.^{1079b, 1567} Its sodium salt poisons cucumber and potato oxidases¹⁰⁷⁰ and inhibits conversion of ammonium ions into nitrite and nitrate.⁹⁹⁵ The substitution of an alkyl for a hydrogen atom of the amino-group in a dithiocarbamic acid increases its hyperglucemic power.^{246b}

Sodium diethylthiocarbamate is active in inhibition of methylene blue respiration in the metabolism of erythrocytes.¹²³⁶ It is a respiratory inhibitor for plant tissues.⁸⁴⁹ Diethylthiocarbamate is a respiratory inhibitor in the phosphate absorption of excised roots²²⁰ and of young barley.¹⁴⁰³ It retarded the photochemical activity of isolated chloroplasts.²⁸

Foliage sprayed with zinc dimethyldithiocarbamate increased the glutamic acid content of sugar beets.⁵⁹⁶ It has superior growth regulatory properties.⁵⁹⁵ Plants grown in nutrient solutions at low levels of manganese and zinc, when sprayed with manganese and zinc dithiocarbamate salts showed increased manganese on the sprayed plants.¹¹⁶⁸ Spraying with fermate increased the yield⁶²⁴ and many demonstrators thought it also stimulated growth.⁵³⁰ Sodium dimethyldithiocarbamate had inhibitory action on spore germination of molds.¹⁵⁰² Derivatives of dithiocarbamates act as fungicides by inhibiting enzyme systems.⁶³⁵

Determination of Dithiocarbamates

The methods for determination of dithiocarbamates have been reviewed.¹²⁷³ The formation of the copper salt, which can be determined photometrically,⁷⁶⁰ can be used to analyze for dithiocarbamates.^{306, 482} A chromatographic analysis serves for the zinc salts, $\text{Zn}(\text{SCSNR}_2)_2$, where R is methyl, ethyl, or butyl.¹²⁶⁵ Various dithiocarbamic acids have been subjected to conductometric titrations using acids, silver nitrate, and iodine.^{1433a} Dithiocarbamate residues on food crops have been determined.^{1053a} The method for determining the manganese salt of ethylene bisdithiocarbamic acid has been given.^{1053b}

To determine a dithiocarbamate in a vulcanization accelerator, the material is distilled with dilute sulfuric acid. The carbon disulfide goes over and is caught in alcoholic potash and titrated with iodine. The amine is liberated and distilled into standard acid. The metal can be estimated.²³¹ The accelerators can be extracted from vulcanized rubber with benzene and identified by the colors they give with copper, nickel, cobalt, and silver reagents in acetic acid solution. The color reactions of thirty-two accelerators are listed.^{1507c, 1508b} The accelerator, carbon tetrachloride, and copper sulfate solution are agitated until a color develops or 1 g. of a finely divided vulcanizate is allowed to stand overnight with 6 cc. of acetone and the copper sulfate added.^{1427a}

Dithiocarbamates can be titrated with a standard nickel sulfate solution using dimethylglyoxime for a spot test.⁹²²

Acids

Salts of Dithiocarbamic Acid as Pesticides

Comparative studies have been made of the effectiveness of dithiocarbamates as fungicides and insecticides.^{758a, 1177, 1370, 1618} Dithio- and bis-dithiocarbamates show antifungal activity.⁹¹⁰ Control methods for orchard diseases have been reviewed.^{479b} It has been suggested that the toxicity of dithiocarbamates is due to their decomposition into amines and carbon disulfide.¹²⁶⁶ This decomposition has been studied.^{1048, 1690} Their fungicidal action has been reviewed.⁹⁰⁹

Sodium dimethyldithiocarbamate is effective against various pests.²⁸ Its fungistatic action is said to be due to combination with copper ions making them unavailable to fungi.¹³²⁴ Metals and chelating agents complex with it for effective fungitoxic action.¹⁵⁰¹ The absorption and fungitoxicity of radioactive potassium dimethyl- and dipropyldithiocarbamate have been studied.¹¹⁹⁸ Experiments on sodium dialkyldithiocarbamates failed to bring forth any correlation between absorption rate and fungistatic action.²⁸⁸

The ferric salt, $(\text{Me}_2\text{N}\cdot\text{CS}\cdot\text{S})_3\text{Fe}$, is known as Fermate or Ferbam and has been used in the control of various plant diseases.^{28, 60, 102, 126, 170, 184, 187, 251, 270, 311, 381, 382, 389, 442, 446, 447a, 479a, 493, 530, 611, 624, 626, 654, 656, 665, 677, 678, 697, 758b, 764, 801, 842, 843, 924, 986, 990, 992a, 1012, 1030, 1073, 1074, 1084, 1085, 1109, 1112, 1144, 1150, 1152, 1153, 1199, 1222, 1223, 1261, 1262, 1269, 1289, 1303, 1307, 1308, 1321, 1341, 1378, 1405, 1418, 1466, 1485, 1518, 1574, 1580, 1581, 1587, 1594, 1600, 1616, 1619, 1690, 1706, 1731a, 1731b, 1746, 1747, 1748, 1749a, 1749c, 1783}

Zerlate, $(\text{Me}_2\text{N}\cdot\text{CS}\cdot\text{S})_2\text{Zn}$,^{140, 320, 329, 381, 389, 546, 563, 758a, 758b, 759, 901, 983, 1012, 1013, 1030, 1110, 1199, 1223, 1378, 1405, 1466, 1518, 1595, 1747, 1749a, 1749b, 1783} and Methasan^{1749a, 1783} a mixture of this zinc salt with Fermate, have attracted some attention. The complex with *c*-hexylamine is an active ingredient in pesticides.^{1075a}

The cadmium, copper, zinc, and sodium dimethyl- and diethyldithiocarbamates have been tested against various insect pests.⁶⁹⁴ The fungicidal and phytocidal properties of sodium, iron, lead, zinc, copper, silver, and mercury dimethyl-, diethyl-, and dibutyldithiocarbamates have been studied.⁶⁴⁰ The sodium, cadmium, zinc, mercury, iron, and copper salts of dithiocarbamic acids,

$RR'N \cdot CS \cdot SH$, have been claimed as bactericides, fungicides, and insecticides.^{221, 320, 1619} Dithiocarbamates are said to be useful in sprays to protect wheat against rust.^{817b}

t-Alkylthio zinc salts are fungicides and insecticides.²²¹ Mono- and dialkyl arsenic salts show bactericidal and fungicidal properties.¹⁶⁵⁰

Sodium pyrrolidine dithiocarbamate has been used in the extraction of heavy metal ions from soil.¹⁵⁵⁸

Heavy metal salts of the dithiocarbamic acid, $O(CH_2CH_2)_2 \cdot N \cdot CS \cdot SH$, derived from morpholine are said to be useful as insecticides and fungicides.^{255a} Water-insoluble salts of certain dithiocarbamic acids can be made dispersible, for use in agricultural spray formations and in rubber latex compounding, by treating with surface-active agents.⁵³⁸ Inorganic sulfite stabilizes solutions of salts.⁸⁶⁹

Disubstituted Dithiocarbamates in Analysis

Dialkyldithiocarbamates react well with salts of metals forming colored bodies which serve to detect very small traces of the metallic salts, especially when the colored compound is extracted with ether or benzene.^{409c} The use of disubstituted dithiocarbamates as precipitants for metals in place of hydrogen sulfide has been reviewed.⁶³² The reactions of thirty-two ions with dithiocarbamates have been described and their sensitivity shown.¹⁰⁹⁶ The use of substituted dithiocarbamates in microchemical analysis has been discussed.^{32, 1097a, 1190}

Diethyl dithiocarbamic acid is a reagent for copper and bismuth.¹⁷⁴¹ It forms complexes with gold and palladium.¹⁴³ The diethylammonium salt can be used for the determination of iron, copper, and manganese.¹⁷⁶⁷ This salt is said to give good results in the colorimetric determination of copper in the presence of lead.¹⁰⁵⁰

Sodium diethyldithiocarbamate, $Et_2N \cdot CS \cdot SNa$, is a valuable analytical reagent.²⁸⁴ It can detect copper ions down to 1 part in 100,000,000 of water.^{229, 409c, 904, 1775} The copper salt has a golden brown color. In dilute solutions the color is proportional to the amount of copper present. It can be extracted from aqueous solutions by *i*-amyl alcohol^{1079a} or by carbon tetrachloride.^{504, 699} By its aid copper can be determined colorimetrically^{229, 291, 304, 325, 403, 482, 641, 661, 699, 710, 775, 833, 856, 975, 982, 985, 1186, 1190, 1239,}

1260, 1271, 1478, 1479, 1490, 1597, 1653, 1658, 1689, 1740 or photometrically.^{222, 306, 308, 492, 622, 699, 702, 739, 796, 798, 1283, 1288, 1605} It is used in the chromatographic analysis of molybdenum, copper, nickel, cobalt, and iron.⁴²

This reagent has been used for the estimation of copper^{736, 863, 1097b, 1232, 1556, 1573, 1729} in distilled water,²²⁹ in drinking water,⁹⁵⁸ in river¹²⁸⁸ and sea^{46, 605} water⁶⁴¹ in distilled liquors,^{622, 1576} in milk,^{325, 1136} in foods,^{313, 400, 465, 661, 762, 1069, 1402, 1568, 1584} in drugs,^{164, 1570} in biological materials,^{553, 889, 942, 985, 1227, 1479, 1560, 1626c} in blood,^{553, 795, 881, 1228, 1408, 1448, 1626b} in blowflies,¹⁶⁸⁵ in plants,^{61, 1227, 1239, 1267, 1339} in fabrics,⁷⁶⁵ in dyes,^{1111, 1260} in rubber,⁴⁰³ in mineral oils,⁹⁶² in spray residues,^{569, 1115, 1238} and other organic materials,¹²⁶⁰ in aluminum,^{107, 1155, 1571, 1653} in steel,^{161, 702, 775, 1476, 1605, 1689} and ferrous alloys,^{702, 739} in lead,⁵⁰⁴ and in phosphorous.¹⁶⁵

It has been employed for zinc,^{46, 144b, 261, 292, 341, 657, 785, 1113b, 1133, 1200, 1351, 1482, 1663, 1704} for lead,^{504, 600, 657, 905, 1200, 1478, 1573, 1626a, 1626b, 1627, 1729} for iron,^{409b, 1234, 1508a, 1775} for cobalt,^{291, 1097b, 1312, 1424} for nickel,^{17, 291, 1097b, 1231, 1424} for mercury,^{1478, 1573, 1591, 1753} for silver,^{1097b, 1478, 1573} for bismuth,^{144c, 282, 929, 1478, 1573} for platinous ion,¹³⁰⁰ for cadmium,^{284, 1573, 1658, 1729} for magnesium,¹¹⁸⁸ for aluminum,¹¹⁴⁹ for arsenic,¹⁵⁷³ for molybdenum,¹⁵⁷³ and for other metals.^{504, 657, 1097b, 1231, 1570}

The sodium salt can be used as an indicator in the detection of traces of copper using an antimony electrode.¹²⁷⁸ Paper impregnated with the sodium or zinc salts may be used for spot tests.³⁰⁵ With osmium tetroxide it gives a violet color.⁶⁷ At pH 4–5 indium is precipitated quantitatively as $(Et_2N \cdot CS \cdot S)_3In$.^{505, 1272} Tellurium⁶⁵² and nickel¹⁷ have been determined photometrically with this sodium salt and tantalum determined colorimetrically.¹⁴⁷⁸ The removal of interfering ions in these determinations has been reported.^{278, 1232} Detailed considerations of the pH and other conditions in these analyses have been discussed.¹⁴⁵ Sulfur dioxide may be estimated by oxidation to the sulfate and analysis for the copper salt.⁸³⁷ This sodium salt can be used for the separation^{2, 1626d} and detection of metal ions by extraction procedures.²

The lead salt has been used to analyze for traces of copper.¹⁶⁵⁵ Silver diethyldithiocarbamate has been used for the photometric

determination of arsenic.¹⁶⁵⁹ It has been used in the analysis of arsine, phosphine, and stibine.¹⁶⁵⁷

Conversely diethylamine and cupric acetate make possible the detection of carbon disulfide^{192, 230, 441, 1615} down to 1–30 γ . Its vapor is absorbed in a mixture of diethylamine and triethanolamine and a solution of copper acetate added.^{31, 516, 517, 1180} A photoelectric colorimeter may be used.¹⁰⁸¹ The reaction with piperidine is so complete that it can be used for the detection and estimation of carbon disulfide.^{258b} This is said to be more accurate than the xanthate method and suitable for detecting 0.01 to 0.07% of carbon disulfide in benzene by the color of the copper salt.⁴²⁰ The sodium salt $(\text{CH}_2)_5\text{N}\cdot\text{CS}\cdot\text{SNa}$, is useful for the quantitative precipitation of copper, cobalt, and zinc ions.^{1507b}

Secondary amines have been analyzed with nickel dithiocarbamates.¹²¹⁷ Dimethylamine has been determined in biological fluids using carbon disulfide and copper sulfate.^{463, 712} Exchange experiments have been made with various metal complexes of N,N-dipropyldithiocarbamates.¹³³⁷

Di(hydroxyethyl)dithiocarbamic acid, $(\text{HOCH}_2\text{CH}_2)_2\text{N}\cdot\text{CS}\cdot\text{SH}$, is a sensitive reagent for copper.^{159, 406, 620} The reagent is made by adding 1 g. carbon disulfide to 10 g. diethanolamine in 85 cc. methanol and diluting to 100 cc.^{159, 620} This acid has been used to mask interfering ions in the determination of ions by the dithizone method.⁸⁹⁴

Sodium cyclohexyl-ethylthiocarbamate detects copper, iron, bismuth, cobalt, and antimony ions in extreme dilution.⁷⁵⁴ The sodium salt of pentamethylenedithiocarbamic acid has been used in metal analysis.¹⁸³ *o*-Aminophenyldithiocarbamic acid has been applied in chromate determinations.⁶⁰¹

Dialkyldithiocarbamates as Vulcanization Accelerators

Various salts of dialkyldithiocarbamic acids are vulcanization accelerators.^{89, 221, 266, 503, 895, 959, 1169c, 1216, 1246, 1296, 1601, 1736a} Zinc salts have received special attention.^{221, 252, 343, 397, 876, 1170a} The zinc salt, $(\text{Me}_2\text{N}\cdot\text{CS}\cdot\text{S})_2\text{Zn}$, induces rapid vulcanization of rubber.^{1183, 1184, 1305, 1410} This and others of its class are claimed as constituents of vulcanization accelerators.^{655, 1017b, 1751a} The zinc and lead salts are powerful accelerators, while the magnesium and calcium are not.^{1129b} The complex of the zinc salt with

c-hexylamine is useful.^{1075a} Zinc salts of dithiocarbamic acids containing furyl and tetrahydrofuryl groups have been patented.^{352b} Zinc and other metal salts of dialkyldithiocarbamic acids are claimed as secondary accelerators.^{1215b, 1215c, 1215d} The cadmium salt, $(\text{Et}_2\text{N}\cdot\text{CS}\cdot\text{S})_2\text{Cd}$, is said to be a vulcanization accelerator.^{1643a} The copper, cobalt, zinc, cadmium, and nickel salts of dibutyldithiocarbamic acid are vulcanization accelerators, the zinc salt being the best.⁶⁰³ A copper dialkyldithiocarbamate is an activator for vulcanization accelerators. The presence of the group $:\text{N}\cdot\text{CS}\cdot\text{S}\cdot$ is beneficial.¹⁵⁴⁴

Alkali salts such as $\text{Bu}_2\text{N}\cdot\text{CS}\cdot\text{SK}$ and $\text{Hep}_2\text{N}\cdot\text{CS}\cdot\text{SNa}$ ^{1736a} and a tertiary cyclohexyl amine salt of a dialkyldithiocarbamic acid are said to aid in vulcanization.^{1169c} Diethylammonium diethyldithiocarbamate is claimed as a constituent of a vulcanization accelerator.³⁹⁴ It has been suggested that this salt can be used in combination with a xanthate.⁵⁵⁴ The reaction product of this salt with ethyl chloroformate is recommended for the same purpose.¹⁶⁴¹ The curing properties of dimethylammonium dimethyldithiocarbamate have been contrasted with the corresponding compound from diethylamine.¹⁴⁴¹ Compounds from alkoxyamines, $(\text{MeOCH}_2\text{CH}_2)_2\text{NH}$, $(\text{EtOCH}_2\text{CH}_2)_2\text{NH}$, $(\text{MeOCH}_2\text{CH}_2\text{CH}_2)_2\text{NH}$, and $(\text{EtOCH}_2\text{CH}_2\text{CH}_2)_2\text{NH}$, and metal salts derived from them are said to be vulcanization accelerators. Some of these salts are balsamic or liquid.³⁹⁹

Di- $\beta\beta$ -alkoxyethylamines have been combined with carbon disulfide. The products, $[(\text{RO})_2\text{CH}\cdot\text{CH}_2]_2\text{N}\cdot\text{CS}\cdot\text{SH}$, and their salts are said to be useful as vulcanization accelerators.^{1541a} Accelerators for low temperature curing are said to be produced from a secondary amine, an aliphatic acid, and carbon disulfide.⁴⁸¹ The products of secondary amine salts with aldehydes, $\text{R}_2\text{N}\cdot\text{CS}\cdot\text{SNR}_2\text{:CHR}'$, are claimed as accelerators.¹⁵³⁷ Various cyclohexyl compounds have been recommended.^{727b, 816a, 822, 1045, 1477, 1531}

Piperidinium pentamethylenedithiocarbamate has been recommended as a vulcanization accelerator,^{82, 89, 449, 1017a, 1063, 1256, 1491} so has its reaction product with ethylchloroformate.¹⁶⁴¹ This can be made by bringing the reactants together in acetone.^{727a} The piperidinium dithiocarbamate solutions are said to be stabilized by water soluble sulfides.^{1750, 1751d} This compound seemed to prevent oxidation between synthesis and compounding.⁶⁵³ Pentamethyleneammonium pentamethylenedithiocarbamate,¹⁵⁷² other

dithiocarbamate compounds, a zinc salt, such as $(\text{Et}_2\text{N}\cdot\text{CS}\cdot\text{S})_2\text{Zn}$, and 2,4-dinitrophenylpentamethylenedithiocarbamate^{1215d} are used along with other compounds as accelerators. The zinc salt, $[(\text{CH}_2)_5\text{NCS}\cdot\text{S}]_2\text{Zn}$, is an activator for a vulcanization accelerator.²¹⁴

Other cyclic imines react similarly. Hexamethyleneammonium hexamethylenedithiocarbamate, $(\text{CH}_2)_6\text{N}\cdot\text{CS}\cdot\text{SN}(\text{CH}_2)_6\text{H}_2$ ^{1215a} and compounds derived from it are claimed as accelerators.^{484b} This salt has been compared with sodium and zinc dibutyldithiocarbamates in the vulcanization of latex films on porous surfaces.¹ The sodium, zinc, cadmium, and lead salts of dimethylenedithiocarbamic acid, $(\text{CH}_2)_2\text{:N}\cdot\text{CS}\cdot\text{SH}$, are claimed as vulcanization accelerators.¹⁷³⁸ Piperidine and carbon selenosulfide react to give piperidinium pentamethyleneselenothiocarbamate which may be used as a vulcanization accelerator.^{1474a}

Miscellaneous Uses

Dialkylammonium dialkyldithiocarbamates, $\text{RR}'\text{N}\cdot\text{CS}\cdot\text{SNH}_2$ - RR' , when added to lubricating oils in small concentrations, are said to permit oxidation and sludge formation.^{99a, 99b} A compound of this type in which R is cyclohexyl and R' either cyclohexyl or some other alkyl is said to homogenize a rust preventive composition.¹⁴⁰⁰

Zinc salts of dialkyldithiocarbamic acids, $(\text{RR}'_2\text{N}\cdot\text{CS}\cdot\text{S})_2\text{Zn}$, in which R and R' may be butyl, amyl, 2-ethylhexyl, or benzyl are claimed as additives to lubricating oils for internal combustion engines.¹⁰⁷¹ Metal and alkylamine salts of dialkyldithiocarbamic acids are said to give antioxidant and detergent properties to the oils.^{422b, 725, 1076, 1761} Oil soluble ferric salts, $(\text{RR}'\text{N}\cdot\text{CS}\cdot\text{S})_3\text{Fe}$, are recommended as stabilizers for lubricating oils.⁴⁶⁴

Tertiary alkylthio zinc dialkyldithiocarbamates,²²¹ tin diamyldithiocarbamate,¹⁰³⁸ and similar salts are claimed as corrosion inhibitors. The compounds from carbon disulfide with piperidine, pipercoline, piperazine, and tetrahydroquinoline are recommended as antioxidants and stabilizers for lubricating oils.^{99a} The zinc salt of pentamethylenedithiocarbamic acid is said to be useful in increasing the resistance of a lubricating oil to oxidation.^{422a} Zinc, cadmium,^{487, 524, 1760} and lead⁵²⁴ salts of various acids are additives for lubricating greases.

Sodium dimethyldithiocarbamate with sodium polysulfide stops

free-radical-initiated emulsion polymerization reactions.³⁴ Metal salts of the acids from piperidine and morpholine added to the mix stops the copolymerization of butadiene and styrene at 50 to 80%.¹⁴⁶⁹ Unsaturated polyamides are improved by heating with sulfur and an accelerator such as the zinc salts of the diethyl- or ethyl-phenyldithiocarbamic acid.³²⁸ Zinc dibutyldithiocarbamate added to rubber is useful as an adhesive on tape.⁹⁵ The copper content controlling action of sodium diethyldithiocarbamate in linoleic acid autooxidation has been investigated.¹⁵²⁶ The dimethylammonium salt of dimethyldithiocarbamic acid is an impregnant for acetylation of cellulose.¹⁶⁰⁶ Sodium diethyldithiocarbamate serves as an antioxidant for butter.¹⁶²³ Dithiocarbamates are conversion agents for the change of *cis*- α,β -unsaturated acids and esters to the *trans* form.^{1474b}

N-Methylglucoseamine reacts with carbon disulfide and alkali to form a polyhydroxyalkyl-alkyldithiocarbamate from which metal salts can be prepared. These are recommended as additions to elastomers and as intermediates for pharmaceuticals.^{812a} The fact that nickel diethyldithiocarbamate, $(\text{Et}_2\text{N}\cdot\text{CS}\cdot\text{S})_2\text{Ni}$, is highly colored may be made use of in photography. A nickel-toned print is treated with sodium diethyldithiocarbamate.¹²²⁹

Wetting agents suitable for mercerization can be obtained from secondary amines with propyl or higher alkyls.^{817c, 1192} Alkali metal dithiocarbamates may be used in froth flotation.¹⁴²³ The effect of sodium diethyldithiocarbamate and *i*-propyl xanthate on pyrite, etc. was studied in relation to its effect on polarizing angles of pyrite, coal, and feldspar.^{1717b}

The *c*-hexyl amine complex with zinc dimethyldithiocarbamate is a deer repellant.⁷⁹

DITHIOURETHANS

These are simply the esters of the dithiocarbamic acids. There are three classes, depending on the extent to which the nitrogen is alkylated:

- | | |
|---|---|
| 1. $\text{H}_2\text{N}\cdot\text{CS}\cdot\text{SH}$ | $\text{H}_2\text{N}\cdot\text{CS}\cdot\text{SR}$ |
| 2. $\text{RHN}\cdot\text{CS}\cdot\text{SH}$ | $\text{RHN}\cdot\text{CS}\cdot\text{SR}'$ |
| 3. $\text{R}_2\text{N}\cdot\text{CS}\cdot\text{SH}$ | $\text{R}_2\text{N}\cdot\text{CS}\cdot\text{SR}'$ |

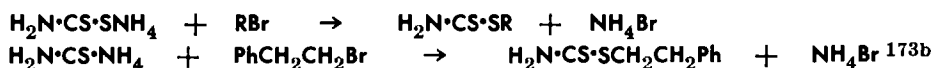
The dithiourethans, being half esters and half thioureas, partake of the properties of both. The thioureas are mostly solids

while the thiocarbonic esters are liquids. Some of the dithiourethans are liquids and others are low melting solids. When the nitrogen is completely alkylated they can be distilled provided the alkyls are not large. These esters show high molecular association provided at least one amino hydrogen remains unsubstituted.²¹⁵

Preparation

Certain preparation methods serve for all three classes while others are for a particular one of the three.

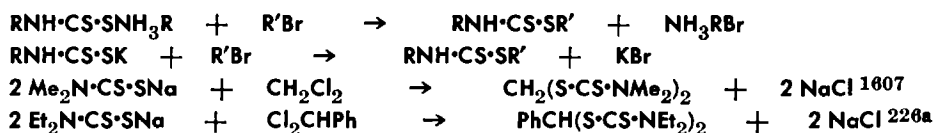
The most generally useful is the alkylation of salts of the acids. As was shown in the last section, these salts are easily procured and, being sulfur compounds, they react readily with alkylation agents. The ammonium salts react well: ^{408b, 413a}



With a reactive halide such as allyl chloride no heating is required. The ammonia, carbon disulfide, and allyl chloride are stirred together in alcohol and cold water added to precipitate the ester: ¹⁷⁷



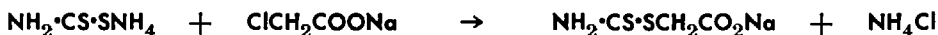
Salts of stronger bases react even more readily:



The halide may be a chlorinated aldehyde,^{1121b} chlorinated cyclohexanone,^{1751c} an α -chlorinated ketone,^{845, 1007b, 1204a, 1372, 1645} or 9-chloroacridone.²⁸⁵ Several chlorosubstituted alkenyl dithiocarbamates such as $\text{Me}_2\text{NCSSCH}_2\text{CH}:\text{CMeCl}$ have been similarly prepared.^{728, 729} Compounds of the formula $\text{R}_2\text{NCSSCH}_2\text{CH}_2\text{NMe}_2$ have been prepared.^{303a, 1538} A number of complex dialkyl dithiocarbamates have been prepared for testing as bactericides.¹³²⁰ Ammonium 2-methyl-4-amino-5-pyrimidylmethyl dithiocarbamate reacts with $\text{AcCHClCH}_2\text{CH}_2\text{OH}$ to give the derivative of vitamin B₁ with an SH group on the 2 position of the thiazole ring.¹⁶²⁴ Complex thiourethans containing the acetyl

and pyrimidyl groups have been prepared.^{767, 768, 841, 1124, 1125, 1769, 1777, 1780, 1781}

Halogenated acids react well. Thus, ammonium dithiocarbamate reacts with a salt of chloroacetic acid: ^{786d, 788a}



The free acid, $\text{NH}_2\cdot\text{CS}\cdot\text{SCH}_2\text{CO}_2\text{H}$, melts at 137° . If it is held there for a minute, gas is evolved and it resolidifies to melt again at 169° . The anhydride has been formed. Anhydride formation takes place if the acid stands in acid solution.^{786d, 788a} This acid inhibits thyroid action.⁴⁵ The sodium salt in acid solution forms rhodanine.⁸⁰² This will be taken up in Volume V. The acids, $\text{R}_2\text{N}\cdot\text{CS}\cdot\text{SCH}_2\text{COOH}$, can be esterified and form amides and phenylhydrazides.^{267b} L-Bromosuccinic acid has been used to prepare the acid, $\text{Et}_2\text{N}\cdot\text{CS}\cdot\text{SCH}(\text{CO}_2\text{H})\text{CH}_2\text{CO}_2\text{H}$.^{887c}

β -Propiolactone adds to ammonium dithiocarbamate or the free acid to give β -dithiocarbamic propionic acid: ^{644b, 666, 667}



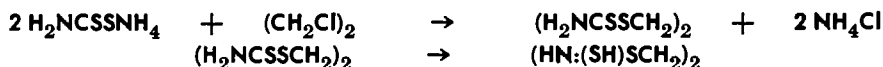
Mono- and di-substituted dithiocarbamic acids give the same reaction. β -Dithiocarbamyl carboxylic acid amides or hydrazides such as $\text{H}_2\text{NC}(\text{S})\text{SCH}_2\text{CH}_2\text{CONH}_2$, are useful as insecticides, fungicides, plant hormones, and polymerization modifiers.^{850c}

Or the amine may be an amino acid and the dithiocarbamate formed alkylated. Carbon disulfide, aminoacetic acid, and alkali give the salt, $\text{KS}\cdot\text{CS}\cdot\text{NHCH}_2\text{COOK}$, from which, with ethyl bromide, the acid, $\text{EtS}\cdot\text{CS}\cdot\text{NHCH}_2\text{CO}_2\text{H}$, can be obtained. The original acid can be esterified to $\text{HS}\cdot\text{CS}\cdot\text{NHCH}_2\text{COOEt}$. The acid $\text{HO}_2\text{C}\cdot\text{CH}_2\text{NH}\cdot\text{CS}\cdot\text{SCH}_2\text{COOH}$ loses water:⁹⁵¹

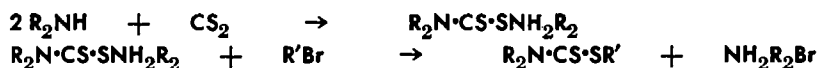


The resulting cyclic compound is a rhodanine.^{787a, 885} Starting with alanine and alkylating with ethyl bromide the acid, $\text{EtS}\cdot\text{CS}\cdot\text{NHCH}(\text{Me})\text{CO}_2\text{H}$, has been prepared. The active forms melt at 107° and the racemic at 114° .^{571b} With chloroacetoacetic acid the dithiocarbamic acid formed reacts further to give ethyl 2-mercapto-4-thiazole acetate. Chloromalonic acid gives a rhodanine.³⁸⁵ α,β -Dihaloethers give bisdithiocarbamic esters which are

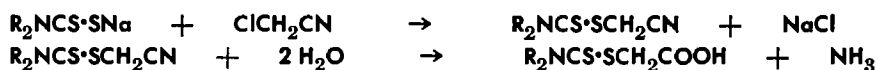
useful for vulcanization accelerators, insecticides, and fungicides.^{1121a} Products claimed to have antibiotic activity for use in plant pathology are obtained by a two step synthesis: (1) treating ammonium dithiocarbamate with an alkyl or aryl dihalide, and (2) rearranging the ester so formed to the dithioisocarbamic ester:¹¹⁷¹



In preparing esters of dialkyldithiocarbamic acids from dialkyl amines it is not necessary to isolate the intermediate salts. The two reactions take place consecutively in the same medium. The secondary amine and the carbon disulfide are put in and the alkyl halide added to the mixture: ^{386, 408a, 408b, 412c, 1541b}



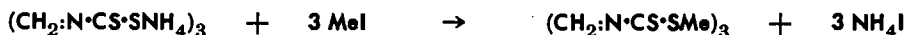
Or the halide may be added to a mixture of the amine, alkali, and carbon disulfide. Both reactions are rapid. When 0.2 moles of carbon disulfide is added dropwise to equivalent amounts of a dialkyl amine and potassium hydroxide in 40 cc. of 75% alcohol, the temperature being kept below 20°, and then an equivalent amount of sodium chloracetate is added, the yield of the acids, $\text{R}_2\text{N}\cdot\text{CS}\cdot\text{SCH}_2\text{CO}_2\text{H}$, is nearly quantitative.^{861b} These acids can also be made from a chloronitrile: ^{267c}



A diazonium salt may react as an alkyl halide: ^{314, 315}

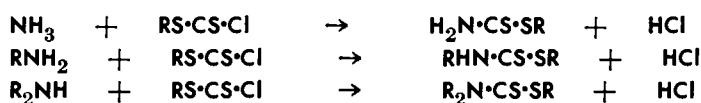


The trimeric ammonium methylenedithiocarbamate gives the methyl ester with methyl iodide: ^{1008a}

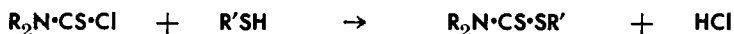


Benzyl chloride reacts with the complexes formed from piperazine and carbon disulfide to form mono- and di-esters.⁴⁷⁸ 1-Bromo-4-methylethylene-*o*-phenylenediarsine reacts with a dithiocarbamic salt.¹¹⁰¹

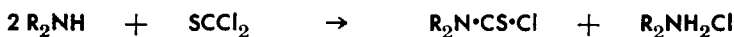
Another general method is the reaction of the dithiocloroformates with ammonia or an amine: ^{171b}



For the N-dialkyl ester the sequence may be reversed: ^{171b, 385, 650, 1363}

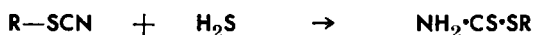


The dialkylthiocarbamyl chloride is from a dialkylamine and thiophosgene: ^{25a, 118a, 119, 172a, 1348}



The utility of these reactions is limited by the difficulty of obtaining thiophosgene. The thiocarbamyl chloride can also be prepared by the action of chlorine on a thiuramdisulfide dispersed in carbon tetrachloride.^{1362a, 1486a} The synthesis of diethyl thiocarbamyl chloride has been given in Organic Syntheses.⁶⁵¹ This compound in carbon tetrachloride adds chlorine to form a perchloride.^{1486b}

An ester of the first class results from the addition of hydrogen sulfide to a thiocyanate: ^{148, 171b, 327, 623, 779d}

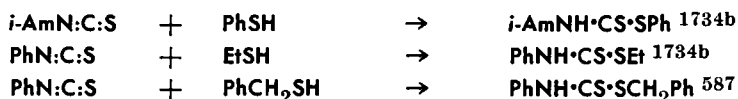


The ethyl ester was prepared in this way by Jeanjean in 1863.^{857a} An alkyl halide is added to a suspension of ammonium thiocyanate in alcohol and hydrogen sulfide passed in.^{408d} Hydrogen sulfide reacts with a cyano group to form a thiocarbamyl group.³³⁶

Esters of the second class result from the addition of a mustard oil to a mercaptan:



This product was not stable and decomposed into its constituents.^{780d}



Certain dialkyldithiocarbamic acids add to acrylonitrile to give β -cyanoethyl dithiocarbamates.^{404a} The reaction with acrylamide is similar.²¹¹ An aliphatic secondary amine, ethylene, and carbon disulfide yield vinyl dithiocarbamates.⁷¹⁵ 2-Mercaptoethyl esters of disubstituted dithiocarbamic acids add to benzo-

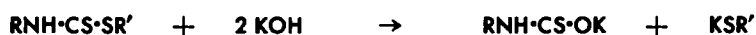
quinone or naphthoquinone to form thioethers in the two position.¹⁶⁸²

Reactions

Dithiourethans, except those that have two alkyls on the nitrogen, are decomposed by heat:



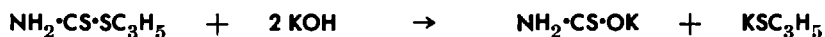
A dithiourethan being an ester can be hydrolyzed:



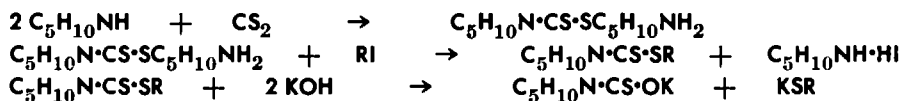
An amine displaces the mercaptan:



The thiourea may, or may not, isomerize to a thiocyanate salt. This depends on the number and character of the substituents. The hydrolysis of a dithiourethan is a preparation method for mercaptans.⁹⁶⁶ Allyl and cinnamyl mercaptans have been made in this way:¹⁷⁷



Mercaptans thus prepared are free from sulfides. Piperidine serves well as the amine:^{172b}



This has been useful for making the higher dithiols. Reference should be made to chapter 1, Volume I. The ketoesters, $\text{MeCOCH}_2\text{SCSNRR}'$, are resistant to acid hydrolysis.^{1204a}

As is well known, an alkyl halide adds to thiourea:



The free base is unstable:



Acting as a modified thiourea, a dithiourethan undergoes analogous reactions:^{857b}



The product is a salt of the base, $\text{NH}:\text{C}(\text{SR})\text{SR}'$, which can be liberated by the addition of the exact amount of alkali. The

free bases are oils which are not stable. They form salts with acids and can be characterized by their picrates. They break up into mercaptans and thiocyanates:



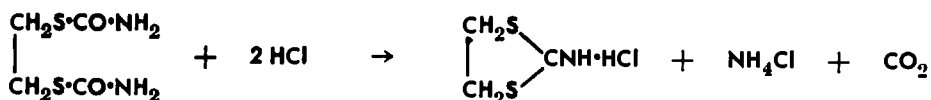
They are decomposed by alkali into a variety of products according to conditions. With nitrous acid nitrogen is eliminated:



This is a method for making dithiolcarbonates; another is the hydrolysis of the salts of these bases: 408a, 408d, 412a



Ethylene-bis-thiourethan reacts with hydrochloric acid:



This forms a silver salt, may be alkylated and acetylated on the nitrogen. The treatment with a primary amine replaces :NH by :NR.¹¹⁶³

The presence of a substituent on the nitrogen influences the nature of the products but does not hinder the reaction with an alkyl halide:



The base $\text{RN:C(SR}'')\text{SR}'$ can be liberated from this salt. The compounds $\text{RN:C(SR}'')\text{SR}'$, are bases and form salts. The picrates crystallize well. They form double iodides, $\text{RN:C(SR}'')\text{SR}'\cdot\text{HgI}\cdot\text{HgI}_2$, with mercuric iodide. They can be reduced by sodium: 407c, 407d, 408a, 412b, 412d, 415a



indicate that the isomerization has taken place.⁷²⁶ The phenylhydrazine derivative of the ethylene ester is converted to ethylene dithiocarbonate by heating with dilute sulfuric acid:²¹⁸



The dialkyl dithiourethans, $\text{R}_2\text{N}\cdot\text{CS}\cdot\text{SR}'$, can not undergo the above reactions, since there can not be a double bond between the nitrogen and carbon atoms. They do not add alkyl halides. They are not basic, do not dissolve in acids, do not form picrates. There is a marked difference between the isomers in physical properties as appears in the data in Table 1.3.^{408b, 412c}

TABLE 1.3

Properties of $\text{R}_2\text{N}\cdot\text{CS}\cdot\text{SR}$ and $\text{RN}:\text{C}(\text{SR})_2$

	<i>B.p.</i>	<i>d</i> 0/4		<i>m.</i>	<i>b.</i>	<i>d</i> 0/4
$\text{MeN}:\text{C}(\text{SMe})_2$	192°	1.1383	$\text{Me}_2\text{N}\cdot\text{CS}\cdot\text{SMe}$	47°	243°	—
$\text{EtN}:\text{C}(\text{SMe})_2$	200.5°	1.0848	$\text{Me}_2\text{N}\cdot\text{CS}\cdot\text{SEt}$	—	252°	1.1255
$\text{MeN}:\text{C}(\text{SEt})_2$	215°	1.0489	$\text{Et}_2\text{N}\cdot\text{CS}\cdot\text{SMe}$	2°	256°	1.0977

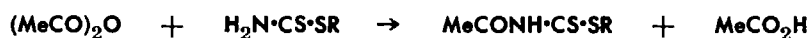
In the three cases where the data are given for both isomers, the esters $\text{R}_2\text{N}\cdot\text{CS}\cdot\text{SR}'$, boil 51° higher than $\text{R}'\text{N}:\text{C}(\text{SR})_2$. The densities are also much higher. The same is true of the melting points. Reduction of the trimethyl ester, $\text{Me}_2\text{N}\cdot\text{CS}\cdot\text{SMe}$, by sodium in alcohol gives trimethylamine, $\text{Me}_2\text{NCH}_2\text{NMe}_2$, methyl mercaptan, and sodium sulfide.^{408b, 412c}

The ultraviolet absorption spectra of $\text{R}_2\text{N}\cdot\text{CS}\cdot\text{SR}$ and $\text{RN}:\text{C}(\text{SR})_2$ ⁸ and the absorption spectra of the methyl esters of dimethyl- and diethyldithiocarbamate⁹⁴⁹ have been investigated.

Unsubstituted dithiourethans are split by sodium into sodium mercaptide and thiocyanate:



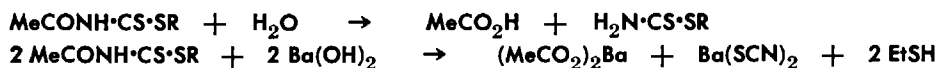
They can be acetylated:^{408d, 413a}



The identical acetyl derivative can be obtained by the addition of thioacetic acid to a thiocyanate:^{272, 289, 1714c, 1715a}



Thiobenzoic acid gives the corresponding benzoate.⁶⁵ This reaction will be taken up in the chapter on thiocyanates in Volume V as a distinctive reaction of thiocyanates.⁸⁷⁰ The acetyl derivative may be hydrolyzed in different ways: ²⁷²



A stepwise degradation of peptides and proteins from the end bearing a free amino group has been accomplished with N-acyldithiocarbamates.⁵⁰² Sodium azide converts an N-substituted dithiocarbamate to a tetrazole.⁹⁰⁶

The exchange between sulfur and methyl diethyldithiocarbamate has been studied in an investigation of accelerators in vulcanization.¹¹⁴⁷

Uses

The reaction product of a salt of a dithiocarbamic acid with dichloroacetic acid or ester is said to be a vulcanization accelerator.^{828, 1016b} Tertiary butyl esters, such as $\text{Et}_2\text{N}\cdot\text{CS}\cdot\text{SCMe}_3$, are recommended for the same use.^{1648a} Various esters of the dimethyl, diethyl, dibutyl, and other dithiocarbamic acids have been cited as accelerators.^{384, 650, 722, 723a, 723b, 729, 827, 1009, 1363, 1486c, 1757} Dithiocarbamate accelerators of the formula $\text{R}_2\text{NCS}\cdot\text{SR}'\text{CH:NR}''$ are prepared by the action of ammonia or amines on the corresponding aldehydo-ester.^{1121b} Carbamylmethyl dimethyldithiocarbamate and pentamethylenedithiocarbamate have been claimed.^{1016a, 1017a} Vulcanization is said to be effected in the presence of a very small percentage of diphenylthiocarbamyl diethylaminomethyl sulfide or other compounds of the general formula, $\text{RSCH}_2\text{NR}'\text{R}''$, in which R is thiocarbamyl and R' and R'' are hydrocarbon radicals.¹⁵²¹

An accelerator results when formaldehyde reacts with a dithiocarbamic acid.^{1017c} The sodium salt of a dialkyldithiocarbamic acid, an ammonium halide, and formaldehyde give products such as $(\text{Ph}_2\text{NCSSCH}_2)_3\text{N}$ which can be used as accelerators.^{878b, 878c} An aldehyde and a naphthol may react with the dialkyldithiocarbamic acid.¹⁷⁵² Monocyclic phenols ^{722, 723b} or an aromatic amine such as aniline ^{723b} combine with formaldehyde, a secondary amine, and carbon disulfide. Tetramethylthiuram disulfide reacts in refluxing acetone to give $\text{Me}_2\text{NCSSCH}_2\text{COCH}_3$,

$(\text{Me}_2\text{NCSSCH}_2)_2\text{CO}$, and $\text{Me}_2\text{NCSSCH}_2\text{C}(\text{NMe}_2):\text{CHSCSN-Me}_2$. These structures have been confirmed by synthesis from chloro- and bromo-acetones.¹³⁷² Formaldehyde and a ketone react with dialkyldithiocarbamic salts to give $\text{RCOCH}(\text{CH}_2\text{S-CS}\cdot\text{NMe}_2)_2$. Acetone may give the double compound, $(\text{Me}_2\text{N-CS}\cdot\text{SCH}_2)_2\text{CHCOCH}(\text{CH}_2\text{S-CS}\cdot\text{NMe}_2)_2$.^{146a} The salt formed from leucauramine and carbon disulfide, on heating in alcohol solution, loses ammonia to form the ester.¹¹⁶⁶ Salts of dithiocarbamic acid react with unsymmetrical dichloroacetone,¹²⁵⁴ with dichloroacetic acid, its esters and amides,⁸²⁶ and with a thiuronium halide^{1751b} to make vulcanization accelerators.

Vinyl esters are used in the preparation of rubber chemicals and insecticides, their polymers are useful in coatings, adhesive, and rubber compounds,⁷¹⁵ and in lubricating oils.^{259b} Butyl dimethyldithiocarbamate and ethylene *bis*-dimethyldithiocarbamate are rubber plasticizers.²⁴² The carboxymethyl ester of this acid is a catalyst for the polymerization of vinylidene compounds.¹³⁴⁶

Allyl dimethyldithiocarbamate, $\text{Me}_2\text{N}\cdot\text{CS}\cdot\text{SC}_3\text{H}_5$,¹⁶¹⁹ and other esters such as $\text{Et}_2\text{N}\cdot\text{CS}\cdot\text{SR}$ in which R is a straight chain radical of 8 to 12 carbon atoms, such as dodecyl, are parasiticides.^{162, 163, 658} These higher esters are also accelerators.¹⁶² The trimethyl ester, $\text{Me}_2\text{N}\cdot\text{CS}\cdot\text{SMe}$, is an effective insecticide.¹⁰⁸⁸ Its homologs $\text{R}_2\text{N}\cdot\text{CS}\cdot\text{SR}$, are useful for combating nematodes.^{818d, 1088} The butoxymethyl ester, $\text{Me}_2\text{N}\cdot\text{CS}\cdot\text{SCH}_2\text{OBu}$, is a pest control agent.^{812c} The dimethylaminomethyl ester is effective against the Mexican bean beetle.⁵³¹

S-Carboxymethyl-N,N-dithiocarbamate and S-(1-carboxy-1-methylethyl)-N,N-dimethyldithiocarbamate check cucumber scab.¹²⁵¹ A parasiticide is said to be produced by the reaction of a primary amine with two moles of an aldehyde and two of dimethyldithiocarbamic acid.^{724, 1651} N-Morpholinomethyl oxydiethylene dithiocarbamate has been tested against lumber mold.⁵³¹ The antifungal activity of N-substituted dithiocarbamic salts and esters has been discussed by Links.¹⁰²⁹

2-Chloroalkyl esters of diethyldithiocarbamic acid have been used for weed control.¹⁶³³ *i*-Propyl dithiocarbamate has a phyto-inhibiting action on wheat seedlings.¹¹³⁸ Some dithiocarbamates prevent the germination of hoed vegetables.¹⁴³⁹ Various plant antibiotics are formed from dithiocarbamic esters.¹³¹⁹ Carboxy-

methyl dimethyldithiocarbamate produced growth responses similar to those brought about by synthetic growth substances.⁹¹⁴

Since the sodium salts of some of the acids are antiseptic their esters were tested.¹³²⁰ 2-Dimethylaminoethyl dimethyldithiocarbamate has been used for treatment of skin diseases.^{303a} This same ester of the dibutyl acid^{1541c} and other dialkyldithiocarbamates²¹⁰ have tuberculostatic activity. The thiocarbamido-type antithyroid drugs may owe their activity to enzymatic inhibition of an oxidase controlling the change from ionic to molecular iodine.⁹⁸⁸ Several dithiocarbamates have been used as intermediates in the manufacture of medicinals, bactericides, and insecticides.¹⁶⁰⁹

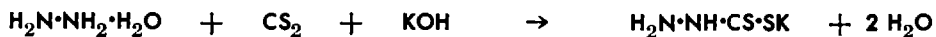
Several dithiocarbamates have been suggested as additives to lubricating oils.^{130a, 130c, 259b, 318, 927, 928, 1391, 1475}

DITHIOCARBAZATES

Carbon disulfide reacts with hydrazine hydrate as with ammonia:



The free acid is too unstable to isolate.^{378, 1141} The salt gives precipitates of the heavy metal salts when it is added to solutions containing the appropriate ions.^{286, 378} The acid may be used as a reagent for silver, bismuth, cadmium, cobalt, cupric, mercuric, nickel, lead, zinc, and cuprous ions.⁶⁸⁷ Ammonium phenyldithiocarbazate serves the same for copper ions.¹⁶¹² Methyl-^{27b} and unsymmetrical dimethylhydrazines¹³⁴⁰ give the analogous compounds. The free dimethylacid, $\text{Me}_2\text{N}\cdot\text{NH}\cdot\text{CS}\cdot\text{SH}$, can be isolated.¹³⁴⁰ Phenyl hydrazine reacts with two molecules of carbon disulfide to form a cyclic compound, $\text{SC}\cdot\text{S}\cdot\text{NPhN}:\text{CSH}$, 'bismuthiol'. This can be used to detect bismuth and $[\text{Fe}(\text{CN})_6]^{-3}$.⁸³² One molecule of hydrazine hydrate, one of alkali, and one of carbon disulfide unite:

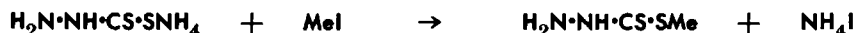


This is readily alkylated.^{50, 216b, 1349} Phenyl hydrazine¹⁵⁶ and substituted phenyl⁶⁸³ hydrazine form these salts. Acid hydrazides will react.^{1420, 1778} With carbon disulfide and potassium hydroxide, ethyl carbazate forms a salt which when alkylated with methyl iodide gives the same compound formed by the reaction of methyl thiocarbazate with ethyl chloroformate:¹⁰⁸⁹



Ammonium dithiocarbazate in solution evaporated to dryness gives the thioanhydride, $\text{S}(\text{CS}\cdot\text{NHNH}_2)_2$. With methyl iodide the dimethyl ether of 2,5-dithio-1,3,4-thiadiazole is formed.^{1049d}

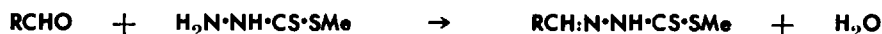
The dithiocarbazate salts react with an alkyl halide to give esters: ^{1049c}



With β -propiolactone the substituted propionic acid is formed. The fully substituted hydrazine, $\text{RR}'\text{NNR}'$, forms a salt which reacts similarly.^{1121c} Phenacyl bromide reacts regularly. Alcoholic chloroacetone with ammonium dithiocarbazate gives a mixture of a thiazolethione and a thiadiazine.^{1417b} α -Chloroacetacetic ester in alcohol solution gives the expected ester. If the solution is evaporated to dryness a thiadiazine is formed. Treating the solution with hydrochloric acid results in a thiazoline.^{1417d} Benzoyldithiocarbazate with chloroacetic acid forms a 3-benzoylamino-rhodanine and an oxadiazole.¹⁴²⁰ The esters of dithiocarbazic acid, $\text{RS}\cdot\text{CS}\cdot\text{NHNH}_2$, when R contains a carboxy group in the α -position are stable only as salts. Acidification of the solution causes the formation of cyclic anhydrides.^{1417c} Alkaline cyclization of these esters gives 1,3,4-oxadiazoles. Acid catalyzed cyclization of 3-acyl dithiocarbazates yields mercaptothiadiazoles.¹⁷⁸⁴ Reduction of methyl *o*-nitrophenyl dithiocarbazate gives 2,3-benzo-6-methylmercapto-1,4,5-triazine hydrochloride.⁶⁸³ *Trans*-phenacyl propyl phenyldithiocarbazate is formed by the action of phenacyl bromide on propyl phenyldithiocarbazate in faintly acid medium. The *cis* compound forms in alkaline medium.¹⁵⁶ The benzyl ester of the same acid reacts with *o*-nitrobenzyl chloride to form benzyl *o*-nitrobenzyldithiocarbonate phenylhydrazone. The *o*-nitrobenzyl ester with benzyl chloride forms its isomer.²¹⁷ Ethyl phenyldithiocarbazate adds to phenyl cyanate:



The esters react with an aldehyde: ^{216b, 1349, 1417b}

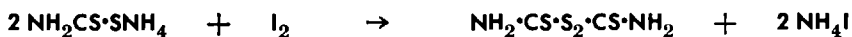


The methyl benzylidene dithiocarbazate melts at 157.5° with decomposition.^{216b}

Thiuram Disulfides, Monosulfides, and Polysulfides

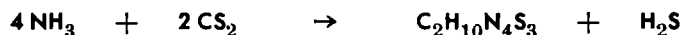
DISULFIDES

In early times ammonium dithiocarbamate was treated with chlorine, bromine, and iodine. The ammonium halides were identified and an unstable solid isolated.^{401b, 1790c} Later it was shown that this is the disulfide, $\text{NH}_2\cdot\text{CS}\cdot\text{S}_2\cdot\text{CS}\cdot\text{NH}_2$, corresponding to dithiocarbamic acid, $\text{NH}_2\cdot\text{CS}\cdot\text{SH}$. The reaction is:



This disulfide is insoluble in water but soluble in acetone, from which it can be precipitated by chloroform as white leaflets, melting at $154-6^\circ$ with decomposition.^{582, 586, 943b} Similar experiments were made with the corresponding salts from methyl and ethyl amines, but on account of the instability of the primary products only those from secondary amines were positively identified.^{779c, 1399}

Hlasiwetz and Kachler⁷⁷⁴ reported a reaction between ammonia and carbon disulfide, in the presence of camphor, benzyl alcohol, or phenol. They wrote the reaction:



This was the diammonium salt of the unstable acid, $\text{H}_4\text{C}_2\text{N}_2\text{S}_3$, or $(\text{H}_2\text{N}\cdot\text{CS})_2\text{S}$. They made several heavy metal salts from the ammonium salt. Their results have been questioned.^{1049a} It has been suggested that their compound was simply ammonium dithiocarbamate, $\text{NH}_2\cdot\text{CS}\cdot\text{SNH}_4$ partly oxidised to thiuram disulfide.⁴⁷¹ It often happens that chemists get quite different results with the same chemicals, under apparently the same conditions. It seems probable that Hlasiwetz and Kachler had what they thought they had, though it is difficult to see how they got it. The compound $(\text{H}_2\text{N}\cdot\text{CS})_2\text{S}$ is the thioanhydride of dithiocarbamic acid and may have the tautomeric formula $\text{S}[\text{C}(\text{:NH})\text{-SH}]_2$. They named the group $\text{H}_2\text{N}\cdot\text{CS}$ —thi-ur-am, taking one syllable each from the words thion, urea, and ammonia. The -am is superfluous since the $-\text{NH}_2$ is a part of the thiourea $\text{NH}_2\cdot\text{CS}\cdot\text{NH}_2$ which they called "thiuramamine." However, the name has stuck; thiuram sulfide and disulfide are: $(\text{H}_2\text{N}\cdot\text{CS})_2\text{S}$ and $(\text{H}_2\text{N}\cdot\text{CS})_2\text{S}_2$. The alkyl derivatives of these are important.

Tetraethylthiuram disulfide is produced quantitatively by the action of iodine on the diethylamine dithiocarbamate: ^{670, 1409}



The same is true of aromatic compounds.⁵⁹¹ The piperidine derivative reacts similarly: ⁴⁹⁷



The monomethyl- and monethylamine derivatives may undergo the normal oxidation: ⁵⁸⁰



The yield from $\text{PhNH}\cdot\text{CS}\cdot\text{SNH}_4$ is poor.^{1049a} Quite different reactions may take place: ^{1049a, 1399}



The disulfides, $\text{RNH}\cdot\text{CS}\cdot\text{S}_2\cdot\text{CS}\cdot\text{NHR}$, are relatively unstable and can not be isolated in every case.^{171a}

In contrast to these, the products from dialkyl amines are stable. The tetramethylthiuram disulfide is an important commercial product. The useful tetraalkylthiuram disulfides are made by oxidising dialkylammonium dithiocarbamates:

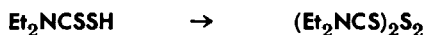


Naturally the sodium salt behaves the same way:

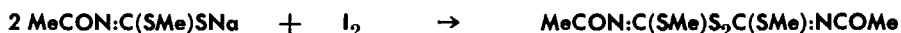


It is not necessary to isolate the dithiocarbamic salts. The amine and carbon disulfide are dissolved in alcohol and the iodine added.^{171a} Bromine,^{171a, 582} hydrogen peroxide,^{4, 171a, 625, 932b} or a persulfate ^{171a, 351, 352a, 836, 1122, 1375, 1742} may be used instead of iodine. Other oxidising agents have been proposed: chlorine,^{287, 331b, 332, 971, 1380a} nitrous acid,^{285, 489, 817a, 971, 1162, 1644} oxides of nitrogen,^{550, 817a, 1044, 1504b} an alkyl nitrite with an inorganic acid,^{1248a} sodium hypochlorite,^{59, 1495b, 1496} a polythionate,^{938, 1504a} ferric chloride,^{471, 582} an electric current,^{608, 1429, 1804} an aryl sulfonyl chloride,⁸³¹ a perborate, or a percarbonate.¹³⁷⁵ A flow process for oxidation of an aqueous solution of sodium diethyldithiocarbamate has been patented.³⁴⁰ Diethylammonium diethyldithiocarbamate in which both sulfur atoms are radioactive

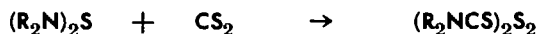
has been prepared starting with radioactive carbon disulfide.⁵⁰⁰ The reaction:



is polarographically irreversible.^{1805b} The polarographic behavior of this oxidation-reduction system has been studied.⁶⁶⁴ The oxidation by nitrous acid is aided greatly by the addition of potassium iodide.¹⁶⁴⁴ Salts of mono- and dithiocarbamic acids are oxidised by chlorine or bromine in the presence of a buffer, sodium carbonate or borax.^{331b} An acetylated thiourethan may be oxidised by iodine in alkaline solution:^{408d}

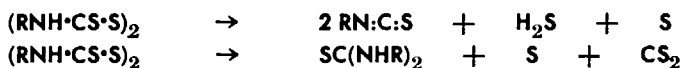


Dialkyl amine sulfides with carbon disulfide form the thiuram disulfides:

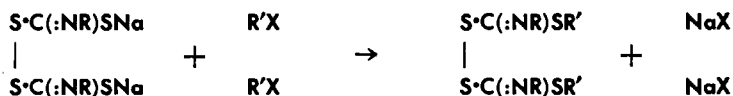


Morpholine disulfide gives the trisulfide.¹²⁸

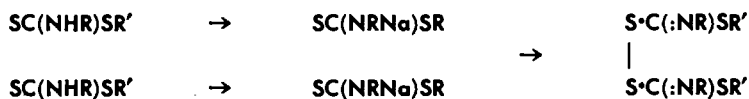
The dialkylthiuram disulfides decompose in two ways on heating, into a mustard oil or into a thiourea: ^{171a, 178}



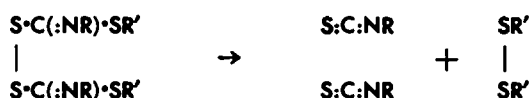
The smaller the alkyls the more mustard oil.^{171a} Tetramethylthiuram disulfide heated to 200° gives carbon disulfide, sulfur, and tetramethyl thiourea. At 150–60° a small amount of dimethylammonium dimethyldithiocarbamate and tetramethylthiuram sulfide are formed. The corresponding tetraethyldisulfide yields chiefly the thiocarbamate salt and carbon disulfide.¹⁴⁰⁹ With sodium ethylate in alcohol they form salts which react with alkyl halides:



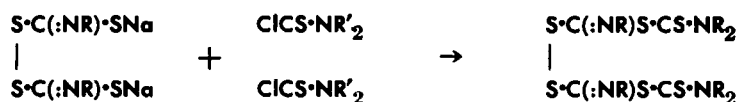
The products are the isothiuram disulfides.^{171a} The same products are obtained by oxidation of dithiourethans in alkaline solution: ^{172a}



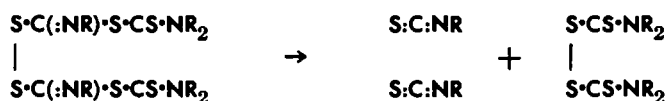
The isothiuram disulfides decompose on warming:



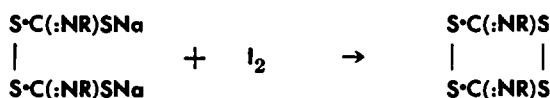
The sodium derivatives of these disulfides react with a thiodialkylcarbamylyl chloride:



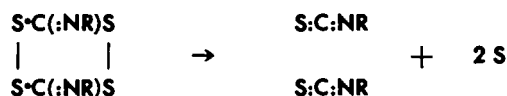
A further reaction takes place:



The sodium derivatives react also with iodine:



The product decomposes into sulfur and a mustard oil: ^{172a, 174}



Tetraalkylthiuram disulfides react with chlorine in carbon tetrachloride to form dialkyl thiocarbamylyl chlorides: ^{1362a, 1486a}



Tetraethylthiuram disulfide forms addition compounds, $(\text{Et}_2\text{NCS})_2\text{S}_2 \cdot 2 \text{CX}_4$, with carbon tetrachloride ⁷⁰⁸ and tetrabromide. ^{391, 708}

Tetramethylthiuram disulfide and dimethylamine in benzene at 100° form dimethylammonium dimethyldithiocarbamate. ^{410c} Dipiperidylthiuram disulfide heated with piperidine to 120° is converted to a mixture of piperidine piperidyldithiocarbamate and dipiperidylthiocarbamide, $\text{SC}(\text{NC}_5\text{H}_{10})_2$. ⁵⁸⁶ There has been a controversy as to the limiting yield of the dithiocarbamate. ^{1434, 1798} Copper bronze reacts with tetraethylthiuram disulfide to form the copper salt of diethyl dithiocarbamic acid. ^{9, 571c} Aryl tellurium gives aryl tellurium salts: ^{561b}



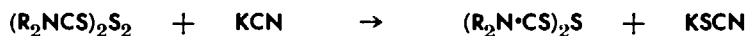
Thiuram disulfides show nucleophilic reactivity similar to that of thio anions with compounds of bivalent selenium and tellurium.^{561b}

Acetic acid and tetramethylthiuram disulfide heated at 125° for five hours decomposes to give carbon disulfide, carbon oxy-sulfide, sulfur, and dimethyl acetamide.³⁴⁶ In refluxing acetone a mixture of compounds results: $\text{Me}_2\text{NHCS}_2\text{CH}_2\text{Ac}$, Me_2NH , CS_2 , $\text{Me}_2\text{NCSSH}\cdot\text{HNMe}_2$, $\text{Me}_2\text{NCS}_2\text{CH}_2\text{C}(\text{NMe}_2):\text{CHS}_2\text{CNMe}_2$, $(\text{Me}_2\text{NCS}_2\text{CH}_2)_2\text{CO}$.¹³⁷²

The exchange of sulfur in polysulfides and vulcanization accelerators has been reviewed.⁶⁹¹ A study has been made of the kinetics of the exchange of radioactive sulfur with thiuram disulfide.^{139, 689} The fact that all of the decomposition products of the tagged thiuram disulfide are radioactive shows the even distribution of the radioactive sulfur.³⁴⁵ This use of the sulfur isotope has been applied to the investigation of vulcanization with tetramethylthiuram mono- and di-sulfides.^{136, 185}

MONOSULFIDES

A remarkable property of the thiuram disulfides is the ease with which they give up half of their sulfur:



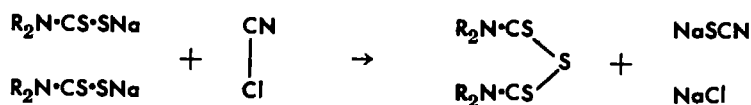
This supplies a method for preparing the monosulfides.^{179, 239} A suspension of the disulfide in water is treated with sodium cyanide solution.¹¹²⁸ The monosulfide can be obtained directly from the dithiocarbamic salt by oxidising it in the presence of a soluble cyanide.¹³⁷⁴ The mechanism of this desulfurization has been studied.²³⁹ Triphenyl phosphorus also removes one sulfur atom:¹⁴⁵⁹



The ease with which sulfur is given up has been given as an explanation of the vulcanizing power of the disulfides, even without free sulfur.^{1380a} Alcoholic potassium cyanide gives the thiourea:¹⁴⁰⁹

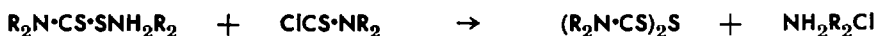


The monosulfides can be prepared directly from dithiocarbamic salts and a cyanogen halide:^{179, 1309b, 1540a}



It may be supposed that sodium chloride and cyanide are formed directly and that the disulfide is desulfurized by the cyanide according to the reaction given above. From the same reactants a dialkylthiuram thiocyanate $\text{RR}'\text{N}\cdot\text{CS}\cdot\text{SCN}$ is said to be obtained.^{309, 1540b} A dispersing agent aids the reaction of cyanogen chloride on the dithiocarbamate salt.^{483c, 1543} Cyanogen bromide gives the trimeric methylenethiuram sulfide, $[(\text{CH}_2:\text{NCS})_2\text{S}]_3$, when it reacts with ammonium methylenedithiocarbamate, $(\text{CH}_2:\text{N}\cdot\text{CS}\cdot\text{SNH}_4)_3$.^{1008a}

Thiuram monosulfides result from the reaction of thiocarbamyl chlorides on salts of dithiocarbamic acids: ^{179, 1362b, 1486a}

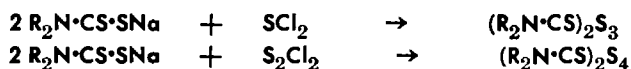


They are obtained also by reacting phosgene with salts of dithiocarbamic acids.^{816d, 824, 1737} A method for preparing tetramethylthiuram monosulfide in a finely dispersed state has been developed.¹²⁰⁵ Aeration of disodium ethylenedisithiocarbamate produces ethylenethiuram monosulfide and polyethylenethiuram monosulfide.¹⁶¹⁰

Tetramethylthiuram sulfide, like the disulfide, heated to 220–280° gives carbon disulfide and tetramethyl thiourea. The corresponding tetraethyl compound at 200–210° yields diethylammonium diethyldithiocarbamate and at higher temperature the thiourea.¹⁴⁰⁹ Chlorination of a monosulfide produces diethyl thiocarbamyl chloride.^{1486a} This chloride adds chlorine to give a perchloride which reacts with more sulfide to increase the yield.^{855, 1486b} Tetramethylthiuram sulfide has been reported to react with bromine to give dimethylcarbamyl dimethylthiocarbamyl sulfide where one group has been oxidised from the thiocarbonyl to the carbonyl group.^{663, 1726}

POLYSULFIDES

The tri- and tetrasulfides are prepared by the reaction of sulfur dichloride or monochloride on salts of dithiocarbamic acids: ^{240, 1006b, 1122, 1377b, 1720a, 1721a, 1721b}



Anabasine, carbon disulfide, and sodium hydroxide combine to give a dithiocarbamate. The zinc salt from this is converted into anabasinethiuram tetrasulfide by sulfur chloride.¹⁰³⁶ In a similar way thiuram tetrasulfides have been prepared from pipercoline¹⁰³⁶ and from heterocyclic imines.²²³

Ammonium phenyldithiocarbamate, $\text{PhNH}\cdot\text{CS}\cdot\text{SNH}_4$, is converted into a polysulfide, $\text{PhN}:\text{C}\cdot\text{S}_8\text{C}:\text{NPh}$, by treatment with sulfur chloride.^{1006c}

DETECTION AND IDENTIFICATION

A number of methods have been proposed. A thiuram disulfide can be reduced with magnesium and sulfuric acid, or by other means. Carbon disulfide is distilled out and the amine left as the sulfate.^{231, 834} Colored complexes with cobalt salts are useful.^{1507a, 1507c, 1508b, 1520} Reduction in the presence of ammonia gives the dithiocarbamate salts, $\text{R}_2\text{N}\cdot\text{CSSNH}_4$ from which nickel salts can be obtained.⁶²⁹ Thiuram compounds are detected colorimetrically by the acetone copper sulfate test^{1472a, 1427b} or by the colored complexes with other copper salts.^{835, 908, 1415, 1508a} Color reactions with copper may be interfered with by anti-aging agents in a vulcanization mix.⁵⁸³ Tetraethylthiuram disulfide can be estimated by bromate-bromide solution.⁵³² Radioactive sulfur may be determined by isolating the dimethyldithiocarbamic acid as its nickel salt and determining its radioactivity.¹³⁹ The monosulfides may be titrated conductometrically with copper sulfate. For the disulfide the titration must be carried out in the presence of hydroquinone.^{1433a} A thiuram compound may be treated with an acetone water solution of potassium cyanide and the resulting potassium thiocyanate titrated with silver nitrate.^{1433b} Chromatographic analysis provides a rapid method for detection of the tetramethyl mono- and di-sulfide and for tetraethylthiuram disulfide; ¹²⁶⁵ methods applicable to raw rubber mixes have been devised.¹³⁸

A sensitive photometric procedure for detecting copper in the presence of other elements is based on the formation of a yellow brown color when copper and tetraethylthiuram disulfide react.¹¹⁴²

PROPERTIES

The absorption spectra of tetramethylthiuram mono- and disulfides have been studied.⁴⁷⁴ Both crystallize in the monoclinic

holohedral system and both have four molecules in the unit cell.¹⁷⁷⁰ The dipole moments of both classes have been determined.⁶⁹⁰

USES

As Vulcanization Accelerators

Comparisons of different thiuram derivatives and suppositions as to the mechanisms of vulcanization by them have been made by a number of investigators.^{88, 90, 137, 185, 204, 212, 330, 343, 344, 346, 373, 475, 508, 523, 853, 877, 896, 959, 978, 994, 1040, 1183, 1184, 1362b, 1380b, 1392, 1431, 1432, 1434, 1435, 1436, 1437, 1489, 1613, 1639, 1640, 1643a, 1643b, 1724} The requirements that must be met by an accelerator have been discussed.^{875, 1129a, 1129b} The special requirements for Buna^{137, 1214} and GR—S⁸⁵ and of mixes containing black factice⁹⁸¹ have been considered. Comparisons have been made of tetramethylthiuram disulfide and of other accelerators as to their influence on the resistivity¹³⁷¹ and on the bonding of the rubber to brass.^{141, 207}

The prevulcanization properties of tetramethylthiuram disulfide have been examined.⁸⁹⁸ Tetramethyl-^{59, 91, 836} and tetraethylthiuram⁸³⁶ disulfides, tetraalkylthiuram sulfides in which the alkyls contain more than four carbon atoms,¹⁶⁴⁹ alkylthiuram sulfides and disulfides^{879a, 879b, 880} and thiuram disulfides in which the alkyl or aryl groups carry constituents^{225a} have been patented as accelerators. Tetramethylthiuram disulfide is known as *Tuads* or *Thionex*, while the monosulfide is called *Monex*. A mixture of 80% tetrabutylthiuram sulfide, 5% thiourea, and 15% urea is recommended.⁹⁷⁶ The thiuram sulfide from cyclohexylethyl amine¹⁰⁴⁵ and the mono- and di-sulfides, $(\text{CH}_2)_6\text{N}\cdot\text{CS}\cdot\text{S}\cdot\text{CS}\cdot\text{N}\cdot(\text{CH}_2)_6$ and $(\text{CH}_2)_6\text{N}\cdot\text{CS}\cdot\text{S}_2\cdot\text{CS}\cdot\text{N}(\text{CH}_2)_6$, from hexamethyleneimine have been claimed.^{484b, 1736b}

It is said that tetraalkylthiuram sulfides and disulfides, containing a total of more than 12 carbon atoms, modify the emulsion polymerization of dienes so that the products are more like natural rubber.^{200b} In polydienes tetramethylthiuram disulfide introduces elemental sulfur into polymers to form disulfide cross links.¹¹³

Very plastic molding compositions containing chloroprene are obtained by milling tetramethylthiuram disulfide into the polymer.¹⁵⁵¹

Tetraalkylthiuram polysulfides have been recommended as

accelerators.^{129b, 1122, 1377b, 1611, 1720a, 1720b, 1721a} A number of these have been compared.¹⁶¹¹ Addition of a small amount of the monosulfide to the polysulfide has been recommended.¹²³⁵ The polysulfides are used with mercaptothiazolines.^{879b} Tetramethylthiuram disulfide with N-c-hexyl-2-benzothiazole sulfenamide gives increased elongation in vulcanized natural rubber.⁸⁹⁷

Zinc and lead salts of thiuram di-, tri-, and tetra-sulfides and of their dimethyl, diethyl, dipropyl, etc. derivatives are vulcanizing agents.^{879c}

Selenium compounds, apparently of the type $R_2N \cdot CS \cdot S \cdot Se \cdot S \cdot CS \cdot NR_2$,¹⁴⁰⁴ and the corresponding tellurium compounds¹²⁰¹ are claimed as accelerators.

As Pesticides

Thiuram sulfides and disulfides, particularly the tetramethyl, have been of considerable interest as constituents of pesticides.⁶²⁸ Data on several hundred sulfur compounds, including a number of thiuram derivatives, as insecticides have been assembled.¹³⁶⁷ Many experiments have been made in the evaluation of thiuram compounds and mixtures containing them.^{19, 448, 694, 696, 731, 1114, 1148a, 1174, 1175, 1266, 1370, 1500, 1603, 1618} There are some patents.^{483b, 552, 695} Thiuram derivatives,^{1619, 1625} particularly the tetraethyl-^{321, 396, 900} are useful in protecting wood and textiles against fungoid growths.

Arasan and Thiosan (later known as Tersan) dusts containing 50% of tetramethylthiuram disulfide, have been investigated extensively.^{37, 184, 244, 249, 251, 311, 329, 335, 360, 361, 362, 369, 398, 443, 447a, 454, 480, 493, 530, 535, 546, 624, 631, 654, 665, 678, 700, 738, 799, 808, 842, 843, 859, 950, 990, 991, 992a, 992b, 993, 1003, 1004, 1014, 1031, 1073, 1074, 1082, 1102, 1118, 1132, 1148b, 1172, 1176, 1220, 1222, 1223, 1224, 1226, 1269, 1303, 1304, 1341, 1465, 1519, 1533, 1557, 1594, 1595, 1608, 1604, 1677, 1743, 1744} Diethylenethiuram di- and trisulfides are said to be fungicides and insecticides.¹¹²² Tetramethylthiuram disulfide has been used as a seed dressing.¹⁸⁰⁶ Carboxymethylthiuram disulfides of the general formula $(HOOCCH_2(R)NCS)_2S_2$ have been claimed.¹⁴²⁶ Dimorpholine-thiuram disulfide has been proposed as the active ingredient of a fungicide.^{255b, 256, 1177}

Tetraethylthiuram sulfide is recommended for internal administration to animals for control of coccidiosis.¹⁶¹⁷ The same compound is effective against scabies.^{393, 647, 648, 899} Tetramethylthi-

uram sulfide and disulfide are used in control of chicken lice.¹⁵⁹⁸

Combinations of heavy metal salts with thiuram disulfides are said to be effective fungicides and seed disinfectants.^{621, 1189} The salt from sodium hydroxide, carbon disulfide, and ethylene or propylene diamine is caused to react with sulfur chloride and the product used as a fungicide.^{757b}

Physiological

The tetraethyl disulfide is quite toxic to microorganisms and invertebrates, possibly because it inactivates copper-containing enzymes.⁷⁰⁸ It is relatively non-toxic to man but gives rise to characteristic unpleasant symptoms if alcohol is subsequently ingested.⁷⁰⁷ The toxicity and action of several thiuram disulfide compounds in alcohol metabolism has been studied.⁹²⁶ Tetraethylthiuram disulfide is toxic to mouse, rat, rabbit, and dog.²⁹⁰ In rats it causes in vivo production of carbon disulfide.¹³¹⁴ Various studies have been made of the effects on experimental animals using it in combination with alcohol.^{43, 44, 709, 845, 933, 984} Its effect when used as therapy in alcoholism is known.¹⁶⁷⁴ While often referred to as antabuse, the name assigned to this drug is 'Disulfiram'.¹⁷⁶² The presence of doubly bound sulfur atoms on two NR_2 groups in the basic nucleus seems essential for disulfiram activity. Unsymmetrical di-*c*-hexylthiocarbamyl diethylthiocarbamyl sulfide, tetrabutylthiuram sulfide, and tetra-*i*-butylthiuram disulfide are as active as disulfiram and less toxic.⁶⁹

The properties and toxicity of tetramethylthiuram disulfide have been studied.⁸⁹³ Its poisonous effect on a man has been described.⁹⁸⁷ A soap containing tetramethylthiuram disulfide has a germicidal action on human skin.⁵⁷ The mono- and disulfides have been added to a waterproofed material to make it actively antiseptic.⁶⁸⁶ The disulfide has been found to be non-toxic to silkworms.⁶²⁷ The toxicity and pharmacological effects of unsymmetrical diethyl dimethylthiuram sulfide on mammals is typically that of any drug inhibiting cholinesterase.⁵⁸ The tetramethylene disulfide activates glycolysis in *Propionibacterium pentosaceum*.²⁶⁸ The influence of tetramethylthiuram disulfide on cellular respiration has been examined.⁴⁹⁵ Tetramethyl-¹³⁹⁷ and tetraethylthiuram^{1342, 1396} disulfides augment the action of pentothal but the tetramethyl compound is twenty times as toxic as the

other.¹³⁹⁷ The in vitro reaction between tetraethylthiuram disulfide and glutathione has been examined.⁸⁷⁵ Thiuram derivatives inhibit *Endothia parasitica*.¹²⁵³

Miscellaneous Uses

The tetramethyl sulfide and disulfide have been claimed as stabilizers and sensitizers for plastic polymers^{916, 1673} and as Diesel dope.³¹⁶ Polystyrene can be protected from degradation by X-ray (Co⁶⁰ source) by tetramethylthiuram disulfide.⁵⁶⁶ Comparatively large amounts have been incorporated in the rubber for manufacture of tooth brushes.¹⁷⁷⁶ The tetramethyl and tetraethyl compounds have been suggested as anti-oxidants for butter.¹⁶²³ *cis*- α,β -Unsaturated acids and esters have been converted to the *trans* compounds by thiuram disulfides.^{1474b}

Physical Properties

The object is to give physical properties, as far as known, of a number of compounds with references to their preparation. No claim is made as to completeness.

As has been said previously, attention is called to the incompleteness and doubtful accuracy of the data and to the desirability of more accurate measurements.

THIOCARBAMIC ACIDS AND SALTS

RR'NCOSH

MeNHCOSH, MeNH₃ salt, m. 121°. ⁵⁸¹

EtNHCOSH, EtNH₃ salt, m. 89°. ³³

i-BuNHCOSH, *i*-BuNH₃ salt, m. 102°. ³³

PhNHCOSH, m. 98°. ¹³⁵⁵

PhN(COPh)COSH, m. 99°. ¹⁷¹¹

PhCH₂NHCOSH, PhCH₂NH₃ salt, m. 125°. ⁷⁰¹

DITHIOCARBAMIC ACIDS AND SALTS

H₂NCSSH, NH₄ salt, m. 145° dec.; ^{1006a} Et₂NH₂ salt, m. 98–105° dec.; Pr₂NH₂ salt, m. 80–90° dec.; *i*-Bu₂NH₂ salt, m. 83–93°. ^{1007c}

(CH₂:NCSSH)₃, (NH₄)₃ salt, m. 154°. ^{1008a}

MeCH:NCSSH, Et₃NH salt, m. 83°; Pr₂NHEt salt, m. 82°; *i*-Bu₂NHEt salt, m. 101°. ^{1007c}

MONOSUBSTITUTED DITHIOCARBAMIC ACIDS

RNHCSSH

- MeNHCSSH, MeNH₃ salt, m. 115°; ^{146b} Et₂NH₂ salt, m. 90°; ^{1707b} piperidine salt, m. 118° dec. ^{146b}
- EtNHCSSH, EtNH₃ salt, m. 103°; ^{780b}, ^{780d} 102°; ³³ Me₂NH₂ salt, m. 101°; ^{1707b} Na salt, m. 98° (4H₂O); Co salt, dec. 66°. ^{323b}
- PrNHCSSH, PrNH₃ salt, m. 102° dec. ⁷⁴²
- BuNHCSSH, Me₂NH₂ salt, m. 93.5°. ^{1707b}
- i*-BuNHCSSH, *i*-BuNH₃ salt, m. 111°. ⁴⁵⁰
- s*-BuNHCSSH, *s*-BuNH₃ salt, m. 109°. ⁴⁵⁰, ^{1196.5}
- i*-AmNHCSSH, *i*-AmNH₃ salt, m. 109°, ^{171a} 100°. ^{778b}
- i*-Undecyl NHCSSH, *i*-Undecyl NH₃ salt, m. 66°. ^{1301a}
- C₁₅H₃₁NHCSSH, C₁₅H₃₁NH₃ salt, m. 99°. ⁸⁵⁸
- Cetyl NHCSSH, Cetyl NH₃ salt, m. 101°. ¹⁶⁷¹
- C₁₇H₃₅NHCSSH, C₁₇H₃₅NH₃ salt, m. 90°. ¹⁶³⁷
- c*-Hexyl NHCSSH, *c* Hex NH₃ salt, m. 160°. ¹⁵¹⁶
- Allyl NHCSSH, Ni salt, m. 135°. ^{323b}
- MeCOCH₂CHMeCH₂NHCSSH, m. 114° dec. ^{851b}
- HOOCCH₂NHCSSH, di NH₄ salt, m. 110° (1 H₂O). ^{27c}
- H₂NCOCH₂NHCSSH, H₃NCH₂COOH salt, m. 139°. ⁷⁸⁴
- EtOOCCH₂NHCSSH, m. 72°; ⁹⁵¹ H₃NCH₂COOEt salt, m. 79°. ^{544a}
- HOOCCHMeNHCSSH, di NH₄ salt, m. 129° dec. (1 H₂O). ^{27c}
- Bornyl NHCSSH, bornyl NH₃ salt, m. 78°. ⁵⁵⁹
- Campholyl NHCSSH, m. 128°; ⁵⁶⁰ campholyl NH₃ salt, m. 96° dec. ⁵⁰⁷
- Quinolyl NHCSSNH₄, 5-, m. 99°; 6-, m. 112°; 8-, m. 87°. ⁵¹⁸
- 4-isoquinolyl NHCSSNH₄, m. 120°. ⁵¹⁸
- 2-Thiazolyl NHCSSH, Et₃NH salt, m. 142°. ⁵¹⁸
- (CH₂NHCSSH)₂, dec. 59°. ¹⁷⁶⁸
- HSCSNHCH₂CH₂N(CH₂CH₂OH)CSSH, di Na salt, m. 101° (5 H₂O). ¹⁸⁹

ArNHCSSH

- PhNHCSSH, NH₄ salt, m. 108° dec.; ⁵⁸² PhNHNH₃ salt, m. 82°. ^{1049b}
- p*-PrC₆H₄NHCSSH, Et₃NH salt, m. 93°. ⁵¹⁸
- p*-BuC₆H₄NHCSSH, Et₃NH salt, m. 92°. ⁵¹⁸
- p*-PhC₆H₄NHCSSH, NH₄ salt, m. 106° dec. ⁸¹

- PhCH₂CH₂NHCSSH, NH₄ salt, m. 132° dec.²⁰⁹
 H₂NC₆H₄NHCSSH, NH₄ salt, *o*, m. 260° dec.; *m*, m. 90°; *p*, m. 250° dec.; ^{1049b} Ac., m. 212–20°.⁵¹⁸
p-Et₂NC₆H₄NHCSSH, *p*-Et₂NC₆H₄NH₃ salt, m. 99°.⁸
 3,4-(MeO)₂C₆H₃CH₂CH₂NHCSSH, NH₄ salt, m. 138° dec.²⁰⁹

FREE ACIDS OR INNER SALTS

- H₂NCH₂CH₂NHCSSH, Na salt, m. 76–80°.¹⁷⁶⁸
 H₂NCHMeCHMeNHCSSH, m. 144° dec.¹⁷⁸⁵
 H₂NCH₂CH₂CH₂CH₂NHCSSH, m. 173°.¹⁵⁶⁹
 H₂NC(:NH)NH(CH₂)₄NHCSSH, m. 210°.¹⁵⁶⁹
 H₂NC(:NH)NH(CH₂)₅NHCSSH, m. 201°.¹⁵⁶⁹
 Et₂NCH₂CH₂NHCSSH, m. 150°.¹⁴⁴³
 Et₂NCH₂CH₂CH₂NHCSSH, m. 150°.¹⁴⁴³
 Et₂NCH₂CH₂CHMeNHCSSH, hemihydrate, m. 138° dec.⁸⁸²
 H₂NCH₂CH₂(Oct) NCSSH, m. 118° dec.¹⁰³⁷
 H₂NCH₂CH₂[(Me₃C)₂CH]NCSSH, m. 146°.¹⁰³⁷
 H₂NCH₂CH₂(C₁₈H₃₇) NCSSH, m. 108° dec.¹⁰³⁷
c-Hex NHCH₂CH₂(*c*-Hex) NCSSH, m. 168° dec.¹⁷⁹⁷
 Et₂NCH₂CH₂(Me) NCSSH, m. 143° dec.,³⁸⁶ 142°.¹⁴⁴³
 Et₂NCH₂CH₂(Et) NCSSH, m. 135° dec.³⁸⁶
 Et₂NCH₂CH₂(*i*-Pr) NCSSH, m. 136°.³⁸⁶
 Et₂NCH₂CH₂CH₂(Me) NCSSH, m. 172°.¹⁴⁴³
 Et₂NCH₂CMe₂CH₂(Me) NCSSH, m. 87°.¹⁴⁴³
 Et₂NCHMeCH₂CHEt(Me) NCSSH, m. 151°.¹⁴⁴³
 Et₂NCH₂CH₂CH₂CHMe(Et) NCSSH, m. 120°.³⁸⁶
 Et₂NCH₂CH₂CH₂CHMe(PhCH₂) NCSSH, m. 151° dec.³⁸⁶
 Et₂NCH₂CH₂CH₂CHMe(*o*-MeOC₆H₄CH₂) NCSSH, m. 128°.³⁸⁶
 Et₂NCH₂CH₂CH₂CHMe[3,4-(MeO)₂C₆H₃CH₂] NCSSH, m. 168°.³⁸⁶
 Et₂N(CH₂)₁₀N(Me)CSSH, 76°.¹⁴⁴³
 Guanidine dithiocarbamic acid, m. 270–80° dec.⁵⁸⁸
 Methyl guanidine dithiocarbamic acid, m. 210–12°.⁵⁸⁸
 1-Methyl guanidine dithiocarbamic acid, m. 255–8°.⁵⁸⁸
 1-Ethyl guanidine dithiocarbamic acid, m. 308–10°.⁵⁸⁸
 Spermine-diguanide dithiocarbamic acid, m. 160–5°.¹⁷⁶³

R₂NCSSH

- Me₂NCSSH, Me₂NH₂ salt, m. 136°,^{146a} 132°,^{1120a, 1409} 125°; *b*. 142°;⁸¹⁵ MeNH₃ salt, m. 91°;^{1707b} *i*-Bu₂NH₂ salt, m. 86°;^{1007c}

- CH₂:NMe₂ salt, m. 40°; ^{1006a, 1537} Na salt, m. 108°; ⁹⁶⁶ As salt, m. 235°; ¹⁶⁰ AsMe salt, m. 144°; ¹⁶⁵⁰ AsMe₂ salt, m. 43°; ¹⁶⁰ AsPh salt, m. 221°; $\overline{\text{C}_6\text{H}_4 \cdot \text{C}_6\text{H}_4 \cdot \text{As}}$ salt, m. 142°; ¹⁶⁵⁰ Cu salt, m. 270°; ⁹ 260° dec.; ^{323b} *p*-MeOC₆H₄Te salt, m. 184° dec.; ^{561b} ZnO(Me₂NCSS)₂Zn, m. 245°. ^{1129b}
- Et₂NCSSH, ionization constant at 25°, $K_a = 2.9 \times 10^{-6}$; ⁶⁶⁴ Et₂NH₂ salt, m. 81°; b. 125°; ¹⁴⁰⁹ EtNH₃ salt, m. 103°; ^{1707b} CH₂:NEt₂ salt, oil; ^{1006a} Sb salt, m. 136°; ¹⁶⁰ As salt, m. 144°; ^{1092c} 135°; AsMe salt, m. 102°; AsMe₂ salt, m. 45°; AsPh salt, m. 140°; AsPh₂ salt, m. 95°; AsC₆H₄OMe salt, *o*, m. 144°; *p*, m. 168°; AsCH:CHCl salt, m. 85°; Bi salt, m. 186°; ¹⁶⁰ dipole moment, 4.05; ⁶⁹⁰ Cd salt, m. 251° dec.; ¹⁷²³ Cr(NO₂)-salt, m. 107°; ^{1093a} Co salt, m. 264°; Cu salt, m. 191°; ^{323b} 190°; ⁹ Pb salt, dipole moment, 2.88; ⁶⁹⁰ Ni salt, m. 236°; ^{323b, 1723} dipole moment, 1.94; ⁶⁹⁰ P salt, m. 120°; ¹⁶⁰ *p*-MeOC₆H₄Te salt, m. 156° dec.; ^{561b} Zn salt, m. 180°; ^{1588, 1591, 1723} dipole moment, 1.89. ⁶⁹⁰
- Pr₂NCSSH, As salt, m. 142°; ^{1092c} Cd salt, m. 160.5°; ¹⁷²³ Co salt, m. 162°; Cu salt, m. 200°; ⁹ 102°; ^{323b} Pb salt, m. 138°; ^{1092a} Ni salt, m. 135.5°; ¹⁷²³ 135°; ²⁶² 130°; ^{323b} Zn salt, m. 114°. ¹⁷²³
- Bu₂NCSSH, Na salt, dipole moment, 3.86 (C₆H₆), 4.9 (dioxane); ⁶⁹⁰ Cd salt, m. 129°; Co salt, m. 122°; Cu salt, m. 114°; ⁹ 90°; ⁶⁰³ Ni salt, m. 91°; ²⁶² 88°; ⁶⁰³ [UO₂(SCSNBu₂)₃]-[H₂NBu₂], m. 153.5°; ¹² Zn salt, m. 108°. ⁶⁰³
- i*-Bu₂NCSSH, Cu salt, m. 165°; ⁹ (UO₂[SCSN(Bu-*i*)₂]₃)[H₂N(*i*Bu)₂], m. 178.5°. ¹²
- i*-Am₂NCSSH, Cu salt, m. 147°; ⁹ [*i*-Am₂NH₂][(i-Bu₂NCSS)₃-UO₂], m. 166°. ¹²
- Me(*i*-Bu)NCSSH, Me(*i*-Bu)NH₂ salt, m. 52°; ¹⁵⁶⁶ [*i*-BuMe-NH₂][(i-BuMeNCSS)₃UO₂], m. 94°. ¹²
- EtPrNCSSH, Cu salt, m. 190°. ⁹
- Me[(Me₂CH)₂CH₂]NCSSH, UO₂ salt, m. 213.5°. ¹²
- $\overline{\text{Me}_2\text{CHCH}_2\text{CHMe}(\text{CH}_2)_2\text{CHCMe}_2\text{NCSSH}}$, UO₂ salt, m. 177°. ¹²
- CH₂(CH₂)₂NCSSH, H₂N(CH₂)₂CH₂ salt, m. 89°. ⁸⁰⁶
- (-CH₂CH₂)₂NCSSH, As salt, m. 255°; ¹⁶⁰ AsMe salt, m. 178°. ¹⁶⁵⁰
- CH₂(CH₂CH₂)₂NCSSH, Me₂NH₂ salt, m. 86°; ^{1007c} CH₂(CH₂-CH₂)₂NH₂ salt, m. 172°; ⁸² 171°; ¹²⁷⁰ dipole moment, 2.48; ⁶⁹⁰ CH₂(CH₂CH₂)₂N:CH₂ salt, m. 61°; ¹⁵³⁷ As salt, m. 248°; ¹⁶⁰ AsMe salt, m. 157°; ¹⁶⁵⁰ Cd salt, m. 257°; Ni salt, m.

- 295.5°; ¹⁷²³ *p*-MeOC₆H₄Te salt, m. 178° dec.; ^{561b} Zn salt, m. 232°.¹⁷²³
- (•CH₂CH₂CH₂)₂NCSSH, (•CH₂CH₂CH₂)₂NH₂ salt, m. 147°; Cd salt, m. 230°; Zn salt, m. 175°.^{1736b}
- O(CH₂CH₂)₂NCSSH, AsMe salt, m. 174°; ¹⁶⁵⁰ AsMe₂ salt, m. 80°.¹⁶⁰
- (HOCH₂CH₂)₂NCSSH, Na salt, m. 155.5°.⁹⁴⁴
- Sorbityl(Me)NCSSH, Na•H₂O salt, m. 155°.^{812a}
- EtOOCCH₂(Me)NCSSH, MeNH₂CH₂COOEt salt, m. 77°; Hg salt, m. 148°.⁵⁶⁵
- PrOOCCH₂(Et)NCSSH, Hg salt, m. 86°.⁵⁶⁵
- MeC₅H₉NCSSH, (pipercoline), Zn salt, m. 194°.¹⁰³⁶
- C₉H₁₁NCSSH, (tetrahydroquinoline), Na salt, m. 77°; Zn salt, m. 202°.¹⁰³⁶
- C₉H₁₁NCSSH, (tetrahydroisoquinoline), Na salt, m. 200°; Zn salt, m. 252°.¹⁰³⁶
- MePhNCSSH, AsMe salt, m. 191°; ¹⁶⁵⁰ Cd salt, m. 295° dec.; ¹⁷²³ Cu salt, m. 245°; ⁹ Ni salt, m. about 300° dec.; Zn salt, m. 254°.¹⁷²³
- EtPhNCSSH, NH₄ salt, m. 110°; ⁷⁴⁵ Cd salt, m. 281°; Ni salt, n. 271°; Zn salt, m. 208°.¹⁷²³
- i*-AmPhNCSSH, Cd salt, m. 222°; Ni salt, m. 196°; Zn salt, m. 247°.¹⁷²³
- Ph₂NCSSH, dipole moment, 4.45.⁶⁹⁰
- (PhCH₂)₂NCSSH, Cu salt, m. 286°.⁹
- (PhCH₂CH₂)₂NCSSH, H₂N(CH₂CH₂Ph)₂ salt, m. 105°; Zn salt, m. 190°.^{1170a}

ACID CHLORIDES AND THIOCYANATES

R₂NCSCI

- Dimethyl-, m. 43.5°; ^{1362b} 43°, ^{1362a} 42°.^{118b}
- Diethyl-, m. 50°; ⁸⁵⁵ 49°, ^{1362a} 48°, ^{1362b} 46.5°; ^{118b} b₁₀ 113°, ^{1362b} 108°, ^{118a} b₅ 81°.^{25a}
- Dipropyl-, b₁₀ 124°.^{118b}
- Di-*i*-propyl-, m. 71°.⁶⁵⁰
- Di-*i*-butyl-, m. 48°.⁶⁵⁰
- Me, Ph-, m. 35°; ^{118a} b₁₉ 152°.¹⁷¹³
- Et, Ph-, m. 57°; ^{171c} 56°.^{1362a}
- Pr, Ph-, m. 36°.¹²¹
- Me, *p*-tolyl-, m. 54°.²³⁹

Et, *o*-tolyl-, m. 69° .²³⁹
 Ethyleneimino-, m. 126° .¹³⁴⁸
 Pyrrolidino-, m. 96° .¹³⁴⁸
 Piperidino-, m. 233° .¹³⁴⁸

$R_2NCSSCN$

Me, Ph-, m. 114° .²³⁹
 Et, Ph-, m. 75.5° .²³⁹
 Me, *p*-tolyl-, m. 116.5° .²³⁹

THIOANHYDRIDES

MeCO·S·CSNH₂, m. 99° , 106° .^{1007b}
 EtCO·S·CSNH₂, m. 94° , 99° .^{1007b}
 MeCO·S·CSNHMe, m. 69° dec.^{146b}
 PhCO·S·CSNHMe, m. 91° .^{146b}
 PhCO·S·CSNHPh, m. 64° .^{172a}
 MeCO·S·CSN(CH₂)₅, m. 61° .^{1007b}
 MeOOC·S·CSNHCH₂CH₂OH, m. 67° .¹⁴⁸³
 EtOOC·S·CSNH₂, m. 99.4° .²⁰⁸
 EtOOC·S·CSNHCH₂CH₂NHCOOEt, dec. 59° .¹⁷⁶⁸
 EtOOC·S·CSNHPh, m. 72° .¹⁴⁶⁸
 ProCS·S·CSNMe₂, m. 44° .^{1540a, 1540c}
i-ProCS·S·CSNMePh, m. 42° .²³⁹
i-ProCS·S·CSNEtPh, m. 41° .²³⁹
 (MePhNCS)₂O, m. 116.5° .^{118a}
 (EtPhNCS)₂O, m. 143.5° .^{118a}
 Me₂NCO·S·CSNMe₂, m. 110° .⁶⁶³
 (Et₂NCSO)₂P(O)OEt, b₁₀-s 101° ; n 20/D 1.5068.¹⁷¹⁸

DISULFIDES

(Me₂NCO)₂S₂, m. 91° ; ⁶⁶³ 4 I, m. 110° .¹²⁷⁰
 (Pr₂NCO)₂S₂, m. 50° .^{172a}
 (Ph₂NCO)₂S₂, m. 196° .^{171c}
 [O(CH₂CH₂)₂NCO]₂S₂, 4 I, m. 85° .¹²⁷⁰

THIURAM MONOSULFIDES

(H₂NCS)₂S, dec. 103° .⁴⁷¹
 (H₂NNHCS)₂S, m. 225° ; crystal change at 170° .^{1049d}
 (Me₂NCS)₂S, m. 110° ,^{944, 1050a, 1050c} 108° ,^{1129a, 1770} 104° ; ¹⁷⁹ di-
 pole moment, 5.29.⁶⁹⁰
 Me₂NCS·S·CSNEt₂, m. 55° .^{1540a, 1540c}

- $(\text{Et}_2\text{NCS})_2\text{S}$, m. 34° ,³⁹⁶ 33° ; d_{20} 1.150.^{1486a}
 $[(\text{CH}_2)_5\text{NCS}]_2\text{S}$, m. 120° ,¹⁷⁹ 116.5° .⁹⁴⁴
 $[(\text{CH}_2)_6\text{NCS}]_2\text{S}$, m. 92° .^{1736b}
 $\text{Me}_2\text{NCS}\cdot\text{S}\cdot\text{CSN}(\text{Et})\text{Ph}$, m. 95° .¹⁷⁹
 $(\text{MePhNCS})_2\text{S}$, m. 151° ; ¹⁷⁹ dipole moment 2.55.⁶⁹⁰
 $(\text{EtPhNCS})_2\text{S}$, m. 115° .¹⁷⁹
 $(\text{Ph}_2\text{NCS})_2\text{S}$, dipole moment, 3.4.⁶⁹⁰
 $[\text{MeS}(\text{PhN:})\text{C}]_2\text{S}$, m. 85° .¹⁷⁹

THIURAM DISULFIDES

- $(\text{MeNHCS})_2\text{S}_2$, m. 102° ,^{171a, 373} 109 dec.⁵⁸¹
 $(\text{EtNHCS})_2\text{S}_2$, m. 79° ,⁵⁸² 75° .^{171a}
 $(\text{PrNHCS})_2\text{S}_2$, m. 58° .^{171a}
 $(i\text{-PrNHCS})_2\text{S}_2$, m. 69° .^{171a}
 $(i\text{-BuNHCS})_2\text{S}_2$, m. 51° .^{171a}
 $(i\text{-AmNHCS})_2\text{S}_2$, m. 62° .^{171a}
 $(\text{EtOOCCH}_2\text{NHCS})_2\text{S}_2$, m. 84° .^{544a}
 $(\text{PhNHCS})_2\text{S}_2$, m. 156° .⁵⁸²
 $(\text{PhCH}_2\text{NHCS})_2\text{S}_2$, m. 71° .^{171a}
 $(\text{Me}_2\text{NCS})_2\text{S}_2$, m. 159° ,^{1129a} 152° ,¹²⁸ 150.5° ,^{331b, 332} 147° ,¹⁷⁷⁰
 146° ; ^{171a, 179, 373, 1619} compound containing S^{35} , m. 156° ; ³⁴⁵
dipole moment, 2.23.⁶⁹⁰
 $(\text{MeEtNCS})_2\text{S}_2$, m. 72° .³⁷³
 $(\text{Et}_2\text{NCS})_2\text{S}_2$, m. 79° ,⁵⁸² 71° ,^{331b, 332} 70.5° ,¹⁵⁰⁹ 70° ; ^{128, 373, 670, 1409}
compound containing S^{35} , m. 70.4° ; ⁵⁰⁰ 2CBr_4 , m. 106° .³⁹¹
 $(\text{Pr}_2\text{NCS})_2\text{S}_2$, m. 50° .^{171a}
 $(i\text{-Pr}_2\text{NCS})_2\text{S}_2$, m. 114° .⁹⁴⁴
 $(i\text{-Bu}_2\text{NCS})_2\text{S}_2$, m. 240° .⁶⁹⁰
 $[(\text{CH}_2)_5\text{NCS}]_2\text{S}_2$, m. 131° ,¹²⁸ 130° ,^{128, 179} 121° ,^{331b, 332} 128.5° .⁹⁴⁴
 $[(\text{CH}_2)_6\text{NCS}]_2\text{S}_2$, m. 110° .^{1736b}
 $[\text{Me}(c\text{-Hex})\text{NCS}]_2\text{S}_2$, m. 106° .^{331b, 332}
 $(\text{MePhNCS})_2\text{S}_2$, m. 198° ,^{171a, 179} 192° ; ³⁷³ dipole moment, 2.55.⁶⁹⁰
 $(\text{EtPhNCS})_2\text{S}_2$, m. 170° .^{171a, 179}
 $(\text{Ph}_2\text{NCS})_2\text{S}_2$, m. 217.6° ; ⁵⁹¹ dipole moment, 3.4.⁶⁹⁰
 $[m\text{-O}_2\text{NC}_6\text{H}_4(\text{Me})\text{NCS}]_2\text{S}_2$, m. 172° .⁵⁹¹
 $[\text{Me}(\text{MeC}_6\text{H}_4)\text{NCS}]_2\text{S}_2$, *o*, m. 200.2° ; *m*, m. 170.5° ; *p*, m. 183° .⁵⁹¹
 $(\text{C}_9\text{H}_{11}\text{NCS})_2\text{S}_2$, (tetrahydroquinoline), m. 74° .¹⁰³⁶
 $(\text{C}_9\text{H}_{11}\text{NCS})_2\text{S}_2$, (tetrahydroisoquinoline), m. 133° .¹⁰³⁶
 $\overline{(\text{CH}_2\text{SO}_2\text{CH}_2\text{CH}_2\text{CHNMeCS})}_2\text{S}_2$, m. 175° .¹⁶⁰¹
 $\overline{(\text{CH}_2\text{SO}_2\text{CH}_2\text{CH}_2\text{CHNEtCS})}_2\text{S}_2$, m. $162\text{--}9^\circ$.¹⁶⁰¹

[HOOCCH₂(Me)NCS₂]S₂, m. 130°. ¹⁴²⁶
 [MeS(MeN)CS]₂, m. 100°; b₁₂ 100°. ^{171a}
 [MeS(HN:)CS]₂, m. 85°. ^{171a}
 [MeS(MeN:)CS]₂, m. 100°; b₁₂ 100°. ^{171a}

THIURAM POLYSULFIDES

(Me₂NCS)₂S₃, dipole moment, 4.80. ⁶⁹⁰
 [O(CH₂CH₂)₂NCO]₂S₃, m. 181°. ^{129b}
 [O(CH₂CH₂)₂NCS]₂S₃, m. 150°, ^{129b} 153°. ¹²⁸
 (Me₂NCS)₂S₄, m. 131°; ^{1006b} dipole moment, 5.78. ⁶⁹⁰
 (Me₂NCS)₂S₆, m. 116°. ⁹⁴⁴
 [(CH₂)₅NCS]₂S₆, m. 140°, ¹²⁸ 129°. ^{1006b}

THIOLCARBAMIC ESTERS

RSCONH₂

Methyl, m. 108°, ^{1712a} 107.5°, ^{1356b} 106°, ⁴¹⁷ 98°; ¹³³ Ac., m. 146°, ^{1714b} 144°. ^{947c}
 Ethyl, m. 109°, ³²⁷ 108°, ^{115, 205, 547, 1356b, 1712a} 102°, ¹²⁹⁷ 100°; ¹³³ Ac., m. 97°. ^{947c}
 Propyl, m. 93°, ^{1352c, 1356b} 91°. ^{75a}
i-Propyl, m. 128.5°, ^{1356b} 125°. ^{1712a}
 Butyl, m. 102°. ^{1356b}
i-Butyl, m. 103.5°, ^{1356b} 103°. ^{1712a}
 Amyl, m. 103.5°. ^{1356a, 1356b}
i-Amyl, m. 113.5°, ^{1356b} 113°, ^{1712a} 107°. ¹⁴⁶²
 Hexyl, m. 105°. ^{1356a, 1356b}
 Heptyl, m. 105°. ^{1356a, 1356b}
 Octyl, m. 105°. ^{1356a, 1356b}
 Nonyl, m. 105.5°. ^{1356a, 1356b}
 Decyl, m. 106.5°. ^{1356a, 1356b}
 Undecyl, m. 107.5°. ^{1356a, 1356b}
 Dodecyl, m. 109.5°, ^{1356b} 109°. ^{1356a}
 Tridecyl, m. 110°. ¹⁴⁴⁹
 Tetradecyl, m. 111°. ^{1356b}
 Pentadecyl, m. 111.5°. ^{1356b, 1449}
 Cetyl, m. 111.5°. ^{1356b}
 Heptadecyl, m. 112°. ¹⁴⁴⁹
 Octadecyl, m. 112°, ¹²⁷ 109°. ^{998a}
 Nonadecyl, m. 113–5°. ¹⁴⁴⁹
 Oleyl, m. 106°. ^{998a}

- c*-Pentyl, m. 139.5°. ^{1356b}
c-Hexyl, m. 112°, ¹⁶⁹³ 104°. ^{1356b}
 PhCOCH₂-, m. 57°. ¹⁵⁸⁶
 Hydnocarpyl, m. 94°. ^{998a}
 Chaulmoogryl, m. 102°. ^{998a}
 HOOCCH₂-, m. 139.5°, ^{786d} 134° dec.; Me ester, m. 80°; Et ester, b. 225° dec.; Am ester, b. 255°.
 PhNHCOCH₂-, m. 149°. ⁵⁷⁶
 MeC₆H₄NHCOCH₂-, *o*, m. 133°; *p*, m. 187°. ¹⁶⁹⁷
 Me₂C₆H₃NHCOCH₂-, 2,6-, m. 160°; 3,4-, m. 157°. ¹⁶⁹⁷
o-PhC₆H₄NHCOCH₂-, m. 159°. ¹⁶⁹⁷
 O₂NC₆H₄NHCOCH₂-, *m*, m. 156°; *p*, m. 190°. ¹⁶⁹⁷
 HOC₆H₄NHCOCH₂-, *o*, m. 184°; *m*, m. 176°; *p*, m. 190°. ¹⁶⁹⁷
p-EtOC₆H₄NHCOCH₂-, m. 177°. ¹⁶³⁶
p-MeCOC₆H₄NHCOCH₂-, m. 196°. ¹⁶⁹⁷
 HOOC₆H₄NHCOCH₂-, *o*, m. 190°; *p*, m. 215°; Et ester, m. 146°. ¹⁶⁹⁷
 2,5-HO(MeO₂C)C₆H₃NHCOCH₂-, m. 205°. ¹⁶⁹⁷
p-HOOCCH₂C₆H₄NHCOCH₂-, m. 194°. ¹⁶⁹⁷
 C₁₀H₇NHCOCH₂-, α, m. 173°, ¹⁶⁹⁷ 164.5°; ¹³⁴⁴ β, m. 197°, ¹⁶⁹⁷ 186° dec. ⁵⁷⁷
 MePhNCOCH₂-, m. 147°, ¹⁶⁹⁷ 143°. ¹³⁴⁴
 EtPhNCOCH₂-, m. 110°. ¹⁶³⁶
 PhCH₂(Ph)NCOCH₂-, m. 144°. ¹⁶⁹⁷
 PhNHNHCOCH₂-, m. 149°. ⁵⁷⁶
 MePhNNHCOCH₂-, m. 147°, ⁸⁷ 146°. ⁵⁷⁶
 HOOCCH₂CH₂-, m. 150°, 149°, ^{850b} 147.5°; ⁹⁷⁹ amide, m. 111°; decyl amide, m. 17.5°; di-Me amide, m. 125°; anilide, m. 136.5°; toluidide, m. 146.5°; *p*-Methoxyanilide, m. 149°. ^{850c}
p-O₂NC₆H₄NHNHCOCH₂CH₂-, m. 204° dec. ^{850c}
 HOOC(CH₂)₁₀-, m. 141°; dodecylthiol ester, m. 99°; decamethylene dithiol ester, m. 114.5°; triglyceride, m. 134°. ¹²⁷
 H₂NCOOCH₂CH₂SCONH₂, m. 111°. ⁶⁸²
 H₂NCOSCH₂SCONH₂, m. 170°. ^{1714b}
 H₂NCOSCH₂CH₂SCONH₂, m. 232°. ^{1714b}
 H₂NCOS(CH₂)₃SCONH₂, m. 179°, ^{1714b} 176.5°. ^{1356b}
 H₂NCOS(CH₂)₄SCONH₂, m. 209°, ^{1352c} 208°. ^{1356b}
 H₂NCOS(CH₂)₅SCONH₂, m. 157.5°. ^{1356b}
 H₂NCOS(CH₂)₁₀SCONH₂, Ac., m. 187°. ¹²⁷
 EtSCONHCONH₂, m. 180° dec. ¹²⁷⁶

i-AmSCONHCONH₂, m. 176°, Ac., m. 85°. ¹⁴⁶²

MeSCONHC(:NH)NH₂, HCl, m. >300°. ¹⁰⁴⁶

ArSCONH₂

Phenyl-, m. 98°, ¹³⁵⁵, ¹³⁵⁸ 97°, ¹⁶⁷² 92°, ^{1365b}

Tolyl-, *o*, m. 139.5°, ¹³⁵⁷ 139°; ^{1352b}, ¹³⁵⁸ *m*, m. 109°, ¹³⁵⁷ 108.5°; ^{1352b},

¹³⁵⁸ *p*, m. 175°. ^{1352b}, ¹³⁵⁷, ¹³⁵⁸

p-HOC₆H₄-, m. 172.5°. ^{1352b}, ¹³⁵⁸

2,5-HOMeC₆H₄-, m. 119°. ¹²⁵⁸

p-MeOC₆H₄-, m. 131°. ^{1352b}, ¹³⁵⁸

p-EtOC₆H₄-, m. 127°. ^{1352b}, ¹³⁵⁸

ClC₆H₄-, *o*, m. 145°; *m*, m. 145.5°; *p*, m. 176° dec. ^{1352b}, ¹³⁵⁸

p-BrC₆H₄-, m. 184°. ^{1352b}, ¹³⁵⁸

p-IC₆H₄-, m. 187° dec. ^{1352b}, ¹³⁵⁸

O₂NC₆H₄-, *m*, m. 124°; *p*, m. 157° dec. ^{1352b}, ¹³⁵⁸

H₂NC₆H₄-, *p*, m. 131°. ^{1352b}, ¹³⁵⁸

p-MeNHC₆H₄-, m. 135°. ^{1352b}, ¹³⁵⁸

p-EtNHC₆H₄-, m. 144°. ^{1352b}

3,4-Me(NH₂)C₆H₃-, m. 136.5°, ¹³⁵⁸ 135.5°. ^{1352b}

Cl(NH₂)C₆H₃-, 2,4-, m. 176° dec.; ^{1352b} 3,4-, m. 159.5°. ¹³⁵⁸

3,4-O₂N(NH₂)C₆H₃-, m. 176°. ¹³⁵⁸

3,4-MeO(NH₂)C₆H₃-, m. 136°. ¹³⁵⁸

p-Me₂NC₆H₄-, m. 131.5°. ^{1352b}, ¹³⁵⁸

p-Et₂NC₆H₄-, m. 108.5°. ^{1352b}, ¹³⁵⁸

p-NCC₆H₄-, m. 165°. ¹³⁵⁸

p-NCSC₆H₄-, m. 199° dec. ¹³⁵⁸

p-HOCC₆H₄-, *m*, m. 184° dec.; ^{1352b}, ¹³⁵⁸ *p*, m. 275–308°, ¹³⁵⁸
300°. ^{1352b}

α-C₁₀H₇-, m. 135.5°. ^{1352b}

p-C₆H₄(SCONH₂)₂, m. 199° dec. ^{1352b}

MONOSUBSTITUTED THIOLCARBAMATES

RNHCOSR'

MeNHCOSR

Butyl-, m. 41°. ¹³⁵⁵

Dodecyl-, m. 49°. ¹³⁵⁵

Phenyl-, m. 104°, ³⁵⁹ 101°. ¹³⁵⁵

Benzyl-, m. 48°. ¹⁶⁹³

HOOCCH₂-, cyclic anhydride, m. 42°. ¹⁶⁹³

2,4-(HO)₂C₆H₃-, m. 139°. ¹²⁵⁸

EtNHCOSR

Methyl-, m. 112°. ⁴¹⁷

Ethyl-, b. 204–8°. ^{780d}

Butyl-, b₁₆ 121°. ¹³⁵⁵

Phenyl-, m. 82°. ^{359, 1487}

HOOCCH₂-, m. 65°. ^{887a}

HOOCCH₂CH(COOH)-, m. 135°; [α]_D 103.5. ^{887d}

(CH₃)₂CHNHCOSR ¹³⁵³

Methyl-, m. 75°.

Ethyl-, m. 60°.

p-Tolyl-, m. 97°.

(•CH₂CH₂-)₂, m. 166°.

p-C₆H₄(SCONHCHMe₂)₂, m. 204°.

C₄H₉NHCOSR

BuNHCOSMe, m. 41°. ¹³⁵⁵

BuNHCOS_{Et}, b₁₆ 121°. ¹³⁵⁵

BuNHCOSCH₂CH₂COOH, m. 105°. ^{850b}

i-BuNHCOSCHPh₂, m. 75°. ¹¹⁰

MeEtCHNHCOS_{Et}, m. 48°. ¹³⁵³

MeEtCHNHCOSC₉H₁₉, m. 46°. ¹³⁵³

t-BuNHCOSMe, m. 88°. ^{1353, 1354}

t-BuNHCOSPh, m. 115°. ^{1353, 1354}

t-BuNHCOSC₆H₄Me-*p*, m. 118°, ¹³⁵⁴ 117°. ¹³⁵³

c-Hexyl NHCOSR

Methyl-, m. 113°. ^{1353, 1354}

Ethyl-, m. 67°. ^{1353, 1354}

Propyl-, m. 45°. ^{1353, 1354}

Butyl-, m. 68°. ^{1353, 1354}

Amyl-, m. 40°, ¹³⁵⁴ 39°. ¹³⁵³

Hexyl-, m. 36°. ^{1353, 1354}

Heptyl-, m. 57°. ^{1353, 1354}

Octyl-, m. 44°, ¹³⁵⁴ 43°. ¹³⁵³

Nonyl-, m. 66°, ¹³⁵³ 65.5°. ¹³⁵⁴

Decyl-, m. 59° .^{1353, 1354}
 Phenyl-, m. 114° ,^{1353, 1354} 113.5° .³⁵⁹
 Tollyl-, *p*, m. 125° .^{1353, 1354}
p-ClC₆H₄-, m. 138° ,¹³⁵⁴ 137° .¹³⁵³
p-BrC₆H₄-, m. 144° .¹³⁵⁴
 (CH₂CH₂-)₂, m. 174° .^{1353, 1354}
 CH₂(CH₂CH₂-)₂, m. 138° .^{1353, 1354}

PhNHCOSR

Methyl-, m. 84° ,^{1734a} 88° .^{1712b}
 Ethyl-, m. 73° .^{1734a}
i-Amyl, m. 67° .¹⁴⁶²
c-Hexyl-, m. 114° .¹³⁵⁵
 HOCH₂CH₂-, m. 60° .⁹⁷
 HOCCCHMe-, m. 117° .^{570a}
 HOCCMe₂-, m. $79-81^{\circ}$, Et ester, m. $79-81^{\circ}$.^{1712b}
 HOCCCH₂CH₂-, m. 152° .⁹⁷⁹
 Phenyl-, m. 122.5° ,^{1365b} 126° .^{359, 1467}
 Benzyl-, m. 97° .^{1707a}
 Tollyl-, *p*, m. 127° .⁷⁸
 PhCH₂CH₂-, m. 110.5° .³⁵⁹
 Ph₂CH-, m. 136° .^{86, 110}

Isobornyl NHCOSR ¹³⁵³

Methyl-, m. 80° .
 Ethyl-, m. 91° .
 Butyl-, m. 36° .
 Amyl-, m. 37° .
c-Pentyl-, m. 111° .
 Phenyl-, m. 90° .
 Tollyl-, *p*, m. 75° .
p-ClC₆H₄-, m. 103° .
 (•CH₂CH₂-)₂, m. 64° .
p-C₆H₄=, m. 173° .

Cl₃CCH(NHCOSR) (NHCOSR')

Dimethyl-, m. 255° .^{1352a}
 Me, Pr, m. 104° .^{1352a}
 Dipropyl-, m. 205° .^{1352a}

Me, Ph, m. 116° .^{1352a}
 Diphenyl-, m. 237.5° ,¹³⁵⁷ 237° ,^{1352a} 221° .¹⁶⁷²
 Ditolyl-, *m*, m. 217° ; *p*, m. 214° .¹³⁵⁷
 (O₂NC₆H₄-)₂, *m*, m. 210° ; *p*, m. 212° .¹³⁵⁷
 (2-C₄H₃S-)₂, m. 178° .^{1352d}

OTHER ALKYL MONOSUBSTITUTED THIOLCARBAMATES

C₁₂H₂₅NHCOSMe, m. 49° .¹³⁵⁵
 AllylNHCOSCHPh₂, m. 116° .¹¹⁰
 OleylNHCOSCH:CHPh, m. 99° .^{998a}
 BzNHCH₂NHCOSBu, m. 161° .¹³⁵³
 BzNHCH₂NHCOSC₇H₁₅, m. 151° .¹³⁵³
 BzNHCH₂NHCOSC₁₀H₂₁, m. 143° .¹³⁵³
 BzNHCH₂NHCOSC₆H₁₁, m. 169° .¹³⁵³
 HOOCCH₂NHCOSPh, m. 155° ,⁴⁹⁸ 154° ; ¹⁰²⁷ acid chloride, m. 87° ; Et ester, m. 104° ,⁴⁹⁸ 106° .¹⁰²⁷
 HOOCCH₂NHCOCH₂NHCOSPh, Et ester, m. 133° .¹⁰²⁷
 HOOCCHMeNHCOCH₂NHCOSPh, Me ester, DL m. 123° .¹⁰²⁷
 HOOCCHMeNHCOSPh, DL, m. 138° ; Me ester, m. 56° .¹⁰²⁷
 HOOCCHMeNHCOCHMeNHCOSPh, DL, Et ester, m. 132° .¹⁰²⁷
 HOOCCH₂CH₂CH(COOH)NHCOSPh, m. 113° ; $[\alpha]_D^{26}$ -22 ± 2 ; anhydride, m. 168° .¹⁰²⁷

ArNHCOSR

m-MeC₆H₄NHCOSEt, m. 59° .²¹⁵
 MeC₆H₄NHCOSCHPh₂, *o*, m. 124° ; *m*, m. 102° ; *p*, m. 151° .⁸⁶
p-MeC₆H₄NHCOSCHMeCOOH, m. 115° .^{570a}
 MeC₆H₄NHCOSPh₂COOH, *o*, dec. 139° ; *m*, dec. 141° ; *p*, dec. 138° .⁸⁶
o-O₂NC₆H₄NHCOSMe, m. 154° .⁴⁹⁹
p-O₂NC₆H₄NHCOSPh, m. 148.8° .³⁵⁹
p-EtOC₆H₄NHCOSPh, m. 145° .³⁵⁹
p-ClC₆H₄NHCOSPh, m. 141.5° .³⁵⁹
o-MeOOC₆H₄NHCOSPh, m. 118.3° .³⁵⁹
 PhCH₂NHCOSCH₂C₆H₄NO₂-*p*, m. 137° .¹⁵⁸³
 C₁₀H₇NHCOSMe, α m. 122° .⁵¹⁵
 C₁₀H₇NHCOSCH₂CH₂COOH, α m. 151° .⁹⁷⁹
 C₁₀H₇NHCOSCHMeCOOH, β m. 156° .^{570a}
 3-(EtSCONH)-dibenzoselenophene-5-oxide, m. 139° .¹⁴²¹

DISUBSTITUTED THIOLCARBAMATES

R'R''NCOSR

Me₂NCOSMe, b. 180°; ^{414b}, ^{415b}, ⁴¹⁷ d 0/4 1.1098, ⁴¹⁷ d 15/4 1.078, d 21/4 1.0904, ^{415b} d 22/4 1.0895, ⁴¹⁷ 1.089; ^{415b} n 21/D 1.50559. ^{415b}

Me₂NCOSBu, b₁₇ 112°. ¹³⁵⁵

Me₂NCOSPh, m. 48°. ¹³⁵⁵

Me₂NCOSCH₂COOH, m. 94°, ¹⁶⁹³ 85°. ^{887a}

Et₂NCOSBu, b₁₆ 145°. ¹³⁵⁵

Bu₂NCOSCH₂CH₂NMe₂, b₂₀ 37–43°; b. 120–40°; EtI, m. 56°. ¹¹³⁹

Am₂NCOSCH₂CH₂NMe₂, Et₂SO₄, m. 56° (½ H₂O); ()₂ Et₂SO₄, m. 125° (1½ H₂O). ¹¹³⁹

c-Hex₂NCOSCH₂CH₂NMe₂, m. 50°; EtI, m. 191°; Et₂SO₄, m. 179°; Et₂SO₄, m. 144° (5½ H₂O); PrI, m. 151°; Pr₂SO₄, m. 139° (6 H₂O); BuI, m. 162.5°; Bu₂SO₄, m. 99.5°; AmI, m. 180°; Am₂SO₄, m. 99–105° (3 H₂O). ¹¹³⁹

(CH₂)₅NCOSBu, b₁₆ 158°. ¹³⁵⁵

(CH₂)₅NCOSPh, m. 62°, ¹³⁵⁵ 60°. ³⁵⁹

HN(CH₂CH₂)₂NCOSC₆H₃(OH)_{2-2,4}, m. 215°. ¹²⁵⁸

α-PyridylCOSPh, m. 152°. ³⁵⁹

MePhNCOSMe, m. 54°, ¹⁰⁸ 48°; b₁₆ 140–2°. ¹⁷¹³

MePhNCOSPh, m. 13°; b₁₉ 160–3°. ¹⁷¹³

MePhNCOSPh, m. 71.5°, ¹⁴⁸⁷ 66.5°. ^{1365b}

EtPhNCOSMe, b₁₇ 149°. ¹⁷¹³

EtPhNCOSPh, m. 97°. ^{1365b}

Ph₂NCOSPh, m. 108°. ⁵¹⁴

Ph₂NCOSC₆H₄Me-*p*, m. 182°. ⁵¹⁴

Ph₂NCOSCH₂Ph, m. 125°. ⁵¹⁴

THIONCARBAMIC ESTERS

ROCSNH₂

Methyl-, m. 43°, ⁷⁴, ⁴¹⁷, ^{1413b} 41°; ^{790c} Ac., m. 80°. ^{1714b}

Ethyl-, m. 41°, ⁷⁴, ¹³², ^{1712b} 38°, ²⁰⁵, ³²⁷, ^{786a}, ^{1413b} 36–9°, ¹²¹³ 36°, ^{971a}, ^{401a} 18°, ¹³³ 16°; d 20/4 1.069; n 20/D 1.520; ^{790c} Ac., m. 104°, ²⁹ 101°; ^{1714b} valerate, m. 56°; ⁴⁵⁰ Bz., m. 74°; ¹⁵¹⁵ *p*-bromobenzoate, m. 99°; ⁴⁹ succinate, m. 167°. ⁴⁵¹

- Propyl-, m. 35° .^{417, 790c}
i-Propyl-, m. 81° ,^{132, 790c} 80° .⁷⁴
 Butyl-, m. 21° ,⁷⁴ 19° .^{790c}
i-Butyl-, m. 53° ,^{74, 1712a} 36° .^{1203a}
i-Amyl-, b. 184° dec.⁸⁶⁸
c-Hexyl-, m. 73.5° ,¹⁶⁹³ 70° ,^{790c} 46° .¹⁵¹⁶
 4-Me-*c*-hexyl-, m. 105° .¹⁵
c-HexCH₂-, m. 76° .¹⁵
 HOCH₂CH₂-, m. 69° .⁷⁴
 ClCH₂CH₂-, m. 107° ,^{1483.5} 106° ; ^{1483.3} Bz., m. 180° .¹⁷⁷²
 HOOCCH₂-, m. 112° ,^{786c, 786d} anhydride, m. 143° .^{786d}
 HOOCCHMe-, L m. $100-15^{\circ}$; $[\alpha]_D^{20}$ 16.6° (abs. calc.).⁷⁴⁷
 Phenyl-, m. 132.5° .^{1365a}
p-ClC₆H₄CH₂-, m. 60° .¹³²
 PhCH₂CH₂-, m. 79° .²⁴¹
 Menthyl-, L m. 145° ; ^{297a, 298a} molecular refractivity in C₆H₆
 259.7° .^{297a}
 Bornyl-, D m. 126° ; ^{298a} L m. 133° ,⁷⁹⁴ 126° ; ^{298a} $[\alpha]_D^{20}$ -2.9° alc; ⁷⁹⁴
 racemic, m. 135.5° .^{298a}
 6-Me-bornyl-, m. 127° .²⁰⁶
 Isobornyl-, m. 131° .¹⁴⁸⁷
 4-Me-isobornyl-, m. 122° .¹⁴⁸⁷
 Dihydrocarvyl-, D m. 63.5° ; $[\alpha]_D$ 135° ; ^{298a} L m. 63° ; $[\alpha]_D$
 -138.89° ; racemic, m. 96° .³⁰⁰
 Fenchyl-, L m. 130° .^{298a}
 Isofenchyl-, 2 forms, oil; ^{1206b} m. 70° ; ^{1206b, 1207} d $15/4$ 0.8134 ; ^{1206b}
 $[\alpha]_D$ -37.77° .^{1206b, 1207}
 (•CH₂CH₂OCSNH₂)₂, m. 209° .^{1352c}

CARBONIC AMIDES OF THIONCARBAMATES

- HOOCNHCSOMe, Me ester, m. 46° ; Et ester, m. 66° .⁴⁵⁵
 HOOCNHCSOEt, Me ester, m. 83° ; ⁴⁵⁵ Et ester, m. 46° ,⁶⁸⁴ 45° ,⁴⁵⁵
 44° ,¹⁷¹⁶ 2 isomeric forms, m. 44° and 144° ; ⁶⁸¹ b₁₃ 135° ; ¹⁷¹⁶
 K salt, m. 225° .⁶⁸⁴
 EtOOCNHCSOPr, m. 32° .⁴⁵⁵
 HOOCNHCSOCH₂Ph, Me ester, m. 67° ; Et ester, m. 103° .⁴⁵⁵

MONOSUBSTITUTED THIONCARBAMATES

Alkyl NHCSOR

- MeNHCSO Hex-*c*, m. 57°. ¹⁶⁹³
 MeNHCSO isofenchyl, m. 70°; $[\alpha]_D$ -37.77°. ¹²⁰⁷
 EtNHCSOEt, b. 204–8°. ^{780d}
 EtNHCSO bornyl, DL m. 67°. ⁷⁹³
 Allyl NHCSOMe, b₁₄ 101–6°. ¹⁴⁵⁴
 Allyl NHCSOEt, b. 210–5°, ^{780d} b₁₄ 115–9°. ¹⁵⁷
 Allyl NHCSOPr, b₁₂ 119–23°. ¹⁴⁵⁴
 Allyl NHCSOPh, m. 51°. ¹⁴⁵⁷
 Allyl NHCSOCHPh₂, m. 61°. ¹¹⁰
 Oleyl NHCSOCH:CHPh, m. 99°. ^{998a}
c-Hexyl NHCSOMe, m. 42°. ²¹⁵
c-Hexyl NHCSOEt, m. 47–50°. ¹²¹³
 MeSO₂CH₂CH₂CH₂NHCSOMe, m. 86°. ¹⁴⁵⁴
 MeSO₂CH₂CH₂CH₂NHCSOEt, m. 71°. ¹⁴⁵⁴
 C₄H₉CH(NHCSOEt)₂, m. 108°. ¹²³
 (•CH₂NHCSOEt)₂, m. 111°. ⁶⁸²
 Tetraacetylglucose NHCSOEt, m. 160°; $[\alpha]_D^{21}$ 11.50 (CHCl₂)₂. ^{544b}
 Tetraacetylallylthiourethan glucoside, m. 99°; $[\alpha]_D^{18}$ -17.92°. ¹⁴⁵⁴
 Tetraacetyl cheirolinthiourethan glucoside, m. 113°; $[\alpha]_D^{20}$ -4.66°
 (CHCl₂)₂. ¹⁴⁵⁴
 Tetraacetyl(PhOCSNH)-D-glucoside, m. 159°; $[\alpha]_D^{15}$ -2.46°. ¹⁴⁵³
 Heptaacetyllactose NHCSOEt, m. 119°. ⁸⁷¹

HOOCCH₂NHCSOR

- Ethyl-, m. 179–86°; ⁹⁴⁸ Et ester, b₁₀ 135–40°. ⁸⁷³
i-Propyl-, m. 129°. ⁹⁴⁸
 Butyl-, m. 71°. ⁹⁴⁸
 Amyl-, m. 50°. ⁹⁴⁸
t-Amyl-, m. 54°. ⁹⁴⁸
 Hexyl-, m. 62°. ⁹⁴⁸
 Heptyl-, m. 66°. ⁹⁴⁸
 Octyl-, m. 72°. ^{48, 948}
 C₁₀H₂₁-, m. 63°. ⁹⁴⁸
 C₁₂H₂₅-, m. 67°. ⁹⁴⁸
 C₁₄H₂₉-, m. 67°. ⁹⁴⁸

Cetyl-, m. 77° .⁹⁴⁸

PhCH₂CH₂CH₂-, m. 88° .⁹⁴⁸

HOOCCHMeNHCSOEt, m. 56° ; b₁₈₋₁₉ $157-9^{\circ}$.^{874b}

PhNHCSOR

Methyl-, m. 97° ,¹²⁵² 96° ,^{1712b} 95° ,¹¹⁹⁵ 94° ,¹¹⁰ 93.5° ,¹³⁹⁸ 93° ; ¹⁵⁷

Ac., m. 49° ; ¹⁷¹³ Bz., m. 95° ; ²¹⁵ 93° .¹⁷¹³

Ethyl-, m. 73° ,^{1712b} 72° ,^{157, 1018} 71° ,¹¹⁹⁵ 69° ,^{63, 114c, 586, 1398} 64° ; ⁶⁸²

Bz., m. 84° .²¹⁵

Propyl-, m. 48° ,¹²⁵² 46° .¹⁵⁷

i-Propyl-, m. 85.5° ,¹²⁵² 85° ,¹⁵⁷ 55° .¹¹⁹⁵

Butyl-, m. 53° .^{157, 460}

i-Butyl-, m. 80.5° ,¹²⁵² 78° ,^{1712b} 76° ,¹⁵⁷ 75° .^{1203a}

t-Butyl-, m. 86.5° .¹⁵⁷

Amyl-, m. 50° .¹⁵⁷

i-Amyl-, m. 46° ,¹⁵⁷ 21° .¹²⁵²

Heptyl-, m. 34° .¹⁵⁷

Octyl-, m. 43° .¹⁵⁷

Nonyl-, m. 47° .¹⁵⁷

c-Hexyl-, m. 80° .³³³

Allyl-, m. 77° ,¹⁵⁷ 65.5° .¹³⁹⁸

MeC:CCH₂-, m. 69.5° .⁵¹¹

MeOCH₂CH₂-, m. 46° .³³³

Et₂NCH₂CH₂-, oil; HCl, m. 122° .¹⁷⁵⁹

Et₂NCH₂CH₂CH₂-, m. 77° ; HCl, m. 100° .¹⁷⁵⁹

4-Morpholinyl CH₂CH₂-, m. 109° ; HCl, m. 156.5° .¹⁷⁵⁹

Phenyl-, m. 142° .¹⁴⁵⁷

Benzyl-, m. 82.5° .¹³⁹⁸

PhCH₂CH₂-, m. 89.5° .¹⁵⁷

PhCH₂CH₂CH₂-, m. 74° .¹⁵⁷

PhCHC₆H₁₃-, m. 147° .³¹⁹

Ph₂CH-, m. 139.5° ,³³³ 136° ,⁸⁶ 125° .¹¹⁰

Menthyl-, L m. 75° ; $[\alpha]_D^{20}$ -63.07° (alc.).¹³⁹⁸

1,2-O-Isopropylideneglyceryl-, m. 40° .³³³

1,3-O-Benzylideneglyceryl-, 2 modifications, m. 159° , 138° .³³³

1,2,3,4-Di-O-isopropylidene galactose, m. 136.5° ; $[\alpha]_D^{20}$ -76.6°
(CHCl₃).³³³

2,3,5,6-Di-O-isopropylidene mannose, m. 116° ; $[\alpha]_D^{20}$ 14.8° .³³³

ArNHCSOR

PhCH₂NHCSOMe, m. 49°. ²¹⁵

MeC₆H₄NHCSOMe, *o*, m. 76°; Bz., m. 92°; *m*, m. 43°; *p*, m. 83°. ²¹⁵

MeC₆H₄NHCSOCHMe₂, *p*, m. 66°. ¹¹⁹⁵ 67°. ¹⁹⁹

MeC₆H₄NHCSOCHPh₂, *o*, m. 124°; *p*, m. 126° dec. ¹¹⁰

BuC₆H₄NHCSOBu, *p*, m. 49°. ¹¹⁹⁵

PhC₆H₄NHCSOEt, m. 117°. ¹⁹⁹

Me₂C₆H₃NHCSOEt, 2,3-, m. 108°; 2,5-, m. 85°; 3,5-, m. 88°. ¹⁹⁹

HOC₆H₄NHCSOBu, *m*, m. 110°; *p*, m. 81°. ¹¹⁹⁵

MeOC₆H₄NHCSOMe, *p*, m. 103°. ²¹⁵

MeOC₆H₄NHCSOEt, *o*, m. 81°. ²¹⁵ 65°; ¹⁹⁹ Bz., m. 104°; ²¹⁵ *m*, m. 85°; *p*, m. 68°; ¹⁹⁹ Bz., m. 89°. ²¹⁵

MeOC₆H₄NHCSOBu, *p*, m. 39°. ¹¹⁹⁵

EtOC₆H₄NHCSOMe, *o*, m. 66°; *p*, m. 81°. ²¹⁵

EtOC₆H₄NHCSOEt, *m*, m. 75°; *p*, m. 95°. ¹⁹⁹ 92-6°. ¹¹⁹⁵

EtOC₆H₄NHCSOBu, *p*, m. 71°. ¹¹⁹⁵

EtOC₆H₄NHCSOAm, *p*, m. 64°. ¹¹⁹⁵

EtOC₆H₄NHCSOC₈H₁₇, *p*, m. 38°. ¹¹⁹⁵

EtOC₆H₄NHCSOCH₂CH₂NEt₂, *p* HCl, m. 146°. ¹¹⁹⁵

BuOC₆H₄NHCSOEt, *p*, m. 66°. ¹¹⁹⁵

BuOC₆H₄NHCSOBu, *p*, m. 49-52°. ¹¹⁹⁵

AmOC₆H₄NHCSOBu, *p*, m. 45°. ¹¹⁹⁵

Allyl OC₆H₄NHCSOMe, *p*, m. 70°. ¹¹⁹⁵

Allyl OC₆H₄NHCSOEt, *p*, m. 65°. ¹¹⁹⁶ 64°. ¹¹⁹⁵

Allyl OC₆H₄NHCSOPr, *p*, m. 59°. ¹¹⁹⁶

Allyl OC₆H₄NHCSOCHMe₂, *p*, m. 64°. ¹¹⁹⁵

Allyl OC₆H₄NHCSOBu, *m*, m. 47°; *p*, m. 48°. ¹¹⁹⁵ 49°. ¹¹⁹⁶

Allyl OC₆H₄NHCSOCH₂CHMe₂, *p*, m. 66°. ¹¹⁹⁵

Allyl OC₆H₄NHCSOAm, *p*, m. 56°. ¹¹⁹⁵

Allyl OC₆H₄NHCSOC₆H₁₃, *p*, m. about 20°; b₇₅₈ 197-9°; n_{23/D} 1.5708. ¹¹⁹⁵

Allyl OC₆H₄NHCSO Allyl, *p*, m. 66°. ¹¹⁹⁶ 65°. ¹¹⁹⁵

Allyl OC₆H₄NHCSOCH₂CH₂NEt₂, *p* HCl, m. 147°. ¹¹⁹⁵

PhOC₆H₄NHCSOBu, *p*, m. 72°. ¹¹⁹⁵

(MeO)₂C₆H₃NHCSOEt, 2,5-, m. 72°; 3,4-, m. 72°; 3,5-, m. 83°. ¹⁹⁹

ClC₆H₄NHCSOMe, *p*, m. 106°. ¹¹⁹⁵

ClC₆H₄NHCSOEt, *m*, m. 82°; *p*, m. 105°. ¹⁹⁹ 102.5°. ⁹⁴

- 2,4-Cl₂C₆H₃NHCSOMe, *m.* 48.5°. ²⁷⁶
 Cl₂C₆H₃NHCSOEt, 2,4-, *m.* 79°; ^{199, 276} 2,5-, *m.* 80°; 3,5-, *m.* 131°. ¹⁹⁹
 2,4-Cl₂C₆H₃NHCSOPr, *m.* 72°. ²⁷⁶
 ClMeC₆H₃NHCSOEt, 2,3-, *m.* 77°; 2,5-, *m.* 59°; 3,2-, *m.* 88°; 3,4-, *m.* 88°; 3,5-, *m.* 105°; 3,6-, *m.* 81°; 4,2-, *m.* 79°; 4,3-, *m.* 101°. ¹⁹⁹
 ClMe₂C₆H₂NHCSOEt, 3,4,6-, *m.* 115°. ¹⁹⁹
 Cl(MeO)C₆H₃NHCSOEt, 3,4-, *m.* 96°; 3,5-, *m.* 86°; 3,6-, *m.* 81°; 4,3-, *m.* 124°. ¹⁹⁹
 FC₆H₄NHCSOEt, *m.* *m.* 84°; *p.* *m.* 86°. ¹⁹⁹
 BrC₆H₄NHCSOEt, *m.* *m.* 94°; *p.* *m.* 107°. ¹⁹⁹
 2,4-Br₂C₆H₃NHCSOEt, *m.* 62°. ²⁷⁶
 2,4-Br₂C₆H₃NHCSOPr, *m.* 68°. ²⁷⁶
 IC₆H₄NHCSOEt, *m.* *m.* 107°; *p.* *m.* 98°. ¹⁹⁹
 O₂NC₆H₄NHCSOMe, *o.* *m.* 68°; ⁴⁹⁹ *m.* *m.* 120°. ¹⁵⁵⁹
 O₂NC₆H₄NHCSOEt, *o.* *m.* 59°; ¹⁹⁹ *m.* *m.* 115°; ^{199, 1422, 1559} *p.* *m.* 178°; ^{846, 1422} 175°. ¹⁹⁹
 O₂N(Me)C₆H₃NHCSOEt, 4,2-, *m.* 95.5°, ¹⁵⁵⁹ 72°; 3,2-, *m.* 110°; 6,2-, *m.* 109°; 4,3-, *m.* 89°; 6,3-, *m.* 112°; 2,4-, *m.* 116°. ¹⁹⁹
 O₂N(MeO)C₆H₃NHCSOEt, 4,2-, *m.* 76°. ¹⁹⁹
 O₂N(F)C₆H₃NHCSOEt, 3,4-, *m.* 118°. ¹⁹⁹
 Me₂NC₆H₄NHCSOCH₂CH₂NEt₂, *p.* *m.* 76°; HCl, *m.* 163°. ¹⁷⁵⁹
 Me₂NC₆H₄NHCSOCH₂CH₂N(CH₂CH₂)₂O, *p.* *m.* 97°; HCl, *m.* 166°. ¹⁷⁵⁹
 Me₂NC₆H₄NHCSOPh, *p.* thiobenzamide, *m.* 122°. ¹³⁶⁸
 NCC₆H₄NHCSOEt, *o.* *m.* 126-9°; ¹¹⁹⁵ *m.* *m.* 95°; *p.* *m.* 110°. ¹⁹⁹
 OCHC₆H₄NHCSOEt, *m.* *m.* 147°; *p.* *m.* 135°. ¹⁹⁹
p-MeCOC₆H₄NHCSOEt, *m.* 111°. ¹⁹⁹
 β-C₁₀H₇NHCSOMe, *m.* 105°. ¹³⁹⁸
 β-C₁₀H₇NHCSOEt, *m.* 97°. ^{338, 1422}
 β-C₁₀H₇NHCSOPr, *m.* 84°. ¹³⁹⁸
 α-C₁₀H₇NHCSOC₁₈H₃₇-2, *m.* 49°. ³³³
 α-C₁₀H₇NHCSOC₆H₁₁, *m.* 110°. ³³³
 α-C₁₀H₇NHCSOCHPh₂, *m.* 163°. ³³³
 C₆H₄(NHCSOEt)₂, *m.* *m.* 116°; *p.* *m.* 197°. ¹²⁰
 MeC₆H₃(NHCSOEt)₂, *m.* 120° (from *m*-toluene isothiocyanate). ¹²⁰

DISUBSTITUTED THIONCARBAMATES

RR'NCSOR''

Me₂NCSOR

Methyl-, m. 3.2°; b₁₀ 68.2°, ^{118c}, ⁴¹⁷ b. 193°, ^{414b}, ^{415b}, ⁴¹⁷ 192°; ¹³⁵
 d 14/2 1.0792, ^{415b} d 15/4 1.0783, ⁴¹⁷ 1.0773, ^{118c}, ⁴¹⁷ 1.078; n 14/D
 1.52657, ^{415b}

Ethyl-, m. 15°, ^{790c} 14.3°; b₁₀ 82.6°, ^{118c}, ⁴¹⁷ b. 206°; d 14/4
 1.0311, ⁴¹⁷ d 15/4 1.0343, ^{118c} 1.0310, ^{415b} d 20/4 1.028; n 20/D
 1.5075, ^{790c} n 14/D 1.51193, ^{415b}

Propyl-, b₁₂ 97°; d 15/4 1.0160, ^{118c}

i-Butyl-, m. 28.8°, ^{118c}

i-Amyl-, b₁₀ 119°; d 15/4 0.9688, ^{118c}

c-Hexyl-, m. -2°; b₈ 136°, ¹⁶⁹³

Phenyl-, m. 30.4°, ^{1365a}

Tolyl-, *o*, m. 55°; *p*, m. 93°, ^{1540a}

o O₂NC₆H₄-, m. 124°, ^{1540a}

Bornyl-, DL m. 112.5°, ⁷⁹³

HOOCCHMe-, D m. 124°; [α]_D -70.2°; solubility in water at 20°
 20.0 g./l.; DL m. 136.7°; Et ester, b₁₅ 146-7°; d 20/4 1.097;
 n 20/D 1.4925, ^{790b}

ESTERS OF OTHER ACIDS

Et₂NCSOMe, b. 210°, ⁴¹⁷ b₁₀ 105.2-5.6°, ^{118c} d 0/4 1.0317, ⁴¹⁷ d
 14/4 1.0192, ^{415b} d 15/4 1.0078, ^{118c} 1.0183; ⁴¹⁷ n 24/D
 1.50670, ^{415b}

Et₂NCSOEt, b₂₀ 114°, ^{717b} b. 224°; ⁴¹⁷ d 15/4 0.9882; n 15/D
 1.50214, ^{415b}

Et₂NCSO bornyl, DL m. 35°, ⁷⁹³

(CH₂)₅NCSOMe, m. 23°; b₁₆ 120-2°, ⁴¹⁷

(CH₂)₅NCSOPr, m. 35°, ⁴¹⁷

3-NO₂-4-pyridyl CSOCHMe, HCl, m. 176°, ¹⁵⁸⁹

3-NO₂-4-pyridyl CSOBu, m. 148°, ¹⁵⁸⁹

MeN(CH₂CH₂)₂NCSOEt, b₃ 117-8°, ⁵⁹³

MePhNCSOMe, b₁₉ 152°, ¹⁷¹³

MePhNCSOEt, b₁₈ 145-50°, ¹⁷¹³

MePhNCSOPh, m. 104°, ^{1365a}

EtPhNCSOMe, m. 42°; b₁₈ 149°, ¹⁷¹³

EtPhNC₂SOEt, m. 18°; b_{12} 143.6°; d_{15} 1.066.¹²¹

EtPhNC₂SOPh, m. 69.2°.¹²¹

C₆H₁₃PhNC₂SOEt, m. 147°.³¹⁹

DITHIOCARBAMATES

RSCSNH₂

Methyl-, m. 42°; ^{171b}, ^{408d}, ^{413a}, ^{415a}, ⁴¹⁷ Ac., m. 119°; ^{408d}, ^{415a}, ^{1715a}

propionamide, m. 108°; ⁵⁰¹ *i*-valeramide, m. 87°; ^{408d}, ^{415a} di-

chloracetamide, m. 125°; ⁵⁰¹ Bz., m. 135°; ^{408d} 134°; ⁵⁰¹ *p*-nitro-

benzamide, m. 104°; 2,4-dichlorobenzamide, m. 127°; 3,5-dini-

trobenzamide, m. 173°; ⁵⁰¹ phenylacetamide, m. 133°; ⁸⁷⁰

PhCH₂OCONHCSSMe, m. 134.5°.⁵⁰¹

Ethyl-, m. 42°; ³²⁷, ^{408d}, ^{413a}, ^{415a} 41°; ²⁷² Ac., ²⁷², ^{408d}, ^{415a} Phenyl-

acetamide, m. 125°.⁸⁷⁰

Propyl-, m. 58°; ^{408d}, ^{413a}, ^{415a}, 57°; ¹⁴⁸ Ac., m. 78°.^{1715a}

i-Propyl-, m. 97°.^{408d}, ^{413a}, ^{415a}, ⁸²³

Butyl-, m. 47°.¹⁷⁴, ¹⁷⁵

t-Butyl-, Ac., m. 113°.^{1714d}

i-Amyl-, m. 51.5°; ¹⁴⁸ Ac., m. 84°.^{1714c}

Hexyl-, m. 50°.¹⁸⁰

Heptyl-, m. 60°.¹⁴⁸

Decyl-, m. 76°.¹⁸⁰

Cetyl-, Ac., m. 90°.^{1715a}

C₁₈H₃₇-, Ac., m. 96°.¹²⁷

Allyl-, m. 32°.^{171b}

MeClC:CHCH₂-, m. 27°.⁷²⁸

Phenyl-, Bz., m. 99°.⁵⁰¹

Benzyl-, m. 90°; ^{408d}, ^{413a} Ac., m. 136°; ^{1715a} 137°; ^{408d} phenylaceta-

mide, m. 123°; ⁸⁷⁰ PhCH₂SCSNHCOOCH₂Ph.⁵⁰¹

PhCH₂CH₂-, m. 66°.^{173b}

PhCH₂CH₂CH₂-, m. 71°.^{173b}

Ph(CH₂)₅-, m. 75°.^{173b}

PhCH:CHCH₂-, m. 124°.¹⁷⁷

p-O₂NC₆H₄CH₂-, m. 135°.^{408d}

MeCOCH₂-, m. 82°.^{1007b}

OHCCCH₂CHMe-, m. 116°.^{851a}

MeCOCH₂CMe₂-, m. 129°.^{851a}

PhCOCH₂-, m. 103°; ^{1007b}, ¹⁶⁴⁵ resolidifies and m. 170°.^{1007b}

MeCOCH₂CHPh-, m. 124°.^{851a}

- PhCOCH₂CHPh-, m. 151°. ^{851a}
 HOOCCH₂-, m. 137°; anhydride, m. 169°; ^{786d, 788a} Bz., m. 156°;
 2,4-dichlorobenzamide, m. 163°. ⁵⁰¹
 HOOCCH₂CH₂-, m. 126°; ^{666, 667} anhydride, m. 120°; ⁶⁶⁷ Et ester,
 m. 66°; Me ester, m. 69.5°; ^{851a} amide, m. 126°; ²¹¹ Zn salt, m.
 145°. ⁶⁶⁶
 HOOCCH₂CH₂CH₂-, Ac., m. 178°; ^{851a} Me ester, m. 69.5°. ^{851a}
 HOOC(CH₂)₁₀-, Ac., m. 100°; dodecyl thioester-, Ac., m. 89°;
 decamethylene dithiolester, di Ac., m. 102.5°; triglyceride, tri-
 Ac., m. 119°. ¹²⁷
 EtOOCCH₂COCH₂-, m. 121°. ^{1007b}
p-MeC₆H₄OCH₂-, Bz., m. 93.5°. ⁶⁵
p-MeOC₆H₄OCH₂-, Bz., m. 106°. ⁶⁵
p-BrC₆H₄OCH₂-, Bz., m. 100°. ⁶⁵
 ClC₆H₄OCH₂-, Bz., *o*, m. 87°; *m*, m. 97°; *p*, m. 96°. ⁶⁵
 Cl₂C₆H₃OCH₂-, 2,4-, Bz., m. 107°; 2,5-, m. 142°. ⁶⁵
 ClMeC₆H₃OCH₂-, Bz., 4,2-, m. 89°; 4,3-, m. 120°. ⁶⁵
p-O₂NC₆H₄OCH₂-, m. 138°. ⁶⁵
 4,2-Cl(O₂N)C₆H₃OCH₂-, m. 150°. ⁶⁵
 α-C₁₀H₇OCH₂-, Bz., m. 115°. ⁶⁵
 2-Cl-pyrimidine-6-acetyl-, m. 284°. ²⁸⁹
 7-Cl-4-quinoline-, m. 148°. ⁶⁰⁶
 CH₂(SCSNH₂)₂, m. 166°; Bz., m. 131°. ^{1715b}
 (-CH₂SCSNH₂)₂, m. 189°. ^{1715b}
 CH₂(CH₂SCSNH₂)₂, m. 176.5°. ^{1356b}
 (-CH₂CH₂SCSNH₂)₂, m. 208°. ^{1356b}
 CH₂(CH₂CH₂SCSNH₂)₂, m. 157.5°. ^{1356b}
 [·(CH₂)₅SCSNH₂]₂, di Ac., m. 159°. ¹²⁷
 (:CHCH₂SCSNH₂)₂, m. 165°. ¹⁷⁶
 O₂S(C₆H₄SCSNH₂-*p*)₂, m. 198° dec. ¹⁰¹⁵

MONOSUBSTITUTED DITHIOCARBAMATES

R'NHCSSR

- MeNHCSSMe, b₂₀ 156°; ^{171b} Ac., b₃₂ 156–8°. ^{408d, 415a}
 MeNHCSSCH₂Ph, m. 80°; Ac., m. 80°. ^{408d}
 MeNHCSSCH₂NHBz, m. 122°. ^{146b}
 MeNHCSSCH₂CH₂CN, m. 38°. ^{404c}
 MeNHCSSCH₂CH₂COOH, m. 85°. ^{404c}
 EtNHCSSEt, b. 210–5°. ^{780d}

EtNHCSSCH₂CH₂CN, m. 91°. ^{404c}

EtNHCSSCH₂CH₂COOH, m. 98°, ⁶⁶⁷ 74°; amide, m. 118°; Et ester, m. 32°. ^{404c}

EtNHCSSCH(COOH)CH₂COOH, DL m. 109°; D m. 113°; [α]_D 55.6°. ^{887b}

i-AmNHCSSEt, b₁₅ 168°. ^{171b}

i-AmNHCSSPh, m. 71°. ^{1734b}

Allyl NHCSSMe, b₂₇ 122°; d 20/4 1.0792; n 20/D 1.5379. ¹³⁹⁸

Allyl NHCSS bornyl, m. 60°. ¹³⁹⁸

HOOCCH₂NHCSSEt, m. 124°; Me ester, m. 75°; Et ester, m 72°. ⁹⁵¹

HOOCCH₂NHCSSOct, m. 100°, ⁹⁴⁸ 99°. ⁴⁸

HOOCCH₂NHCSSC₁₂H₂₅, m. 111°. ⁹⁴⁸

HOOCCHMeNHCSSEt, DL m. 114°; active, m. 107°. ^{571b}

2-Thiazolyl NHCSSMe, m. 185°. ⁵¹⁸

Campholyl NHCSSMe, m. 147°. ⁵⁶⁰

(-CH₂NHCSSCH₂CH₂CONH₂)₂, m. 189°. ²¹¹

PhNHCSSR

Methyl-, m. 96°, ¹³⁹⁸ 93.5°, ^{1049a} 88°. ^{1734a}

Ethyl, m. 61°, ¹³⁹⁸ 60°, ^{1734b} 59.5°; ^{1049a} dipole moment 3.20. ⁶⁹⁰

Propyl-, m. 67°. ¹³⁹⁸

i-Amyl-, m. 71°. ^{1734b}

Allyl-, m. 42°. ^{171b}

EtOOCCH₂-, m. 63°. ^{171b}

HOOCCH₂CH₂-, m. 154°; ^{788c} amide, m. 140°. ²¹¹

Phenyl-, m. 106°. ^{1365b}

Benzyl-, m. 85°. ⁵⁸⁷

o-O₂NC₆H₄CH₂-, m. 121°. ^{27d}

Ph₂CH-, m. 130°. ¹⁵⁵²

PhCH₂NHCSSR

Methyl-, m. 57°. ²¹⁵

Ethyl-, m. 52°. ²¹⁵

NCCH₂CH₂-, m. 54°. ^{404c}

HOOCCH₂CH₂-, m. 94°; amide, m. 158°; ^{404c} 159°; ²¹¹ Benzyl ester, oil. ^{404c}

p-O₂NC₆H₄CH₂-, m. 91°; Bz., m. 114°. ¹⁵⁸³

Other ArNHCSSR

- $\text{PhCH}_2\text{CH}_2\text{NHCSSCH}_2\text{CH}_2\text{CN}$, m. 54° .^{404c}
 $\text{PhCH}_2\text{CH}_2\text{NHCSSCH}_2\text{CH}_2\text{CONH}_2$, m. 139° .^{404c}
m- $\text{MeC}_6\text{H}_4\text{NHCSSEt}$, m. 63° .²¹⁵
o- $\text{EtC}_6\text{H}_4\text{NHCSSMe}$, m. 75° .²¹⁵
p- $\text{PrC}_6\text{H}_4\text{NHCSSMe}$, m. 69° .⁵¹⁸
p- $\text{BuC}_6\text{H}_4\text{NHCSSMe}$, m. 71° .⁵¹⁸
 $2,4\text{-Me}_2\text{C}_6\text{H}_3\text{NHCSSMe}$, m. 103° .²¹⁵
 $2,4\text{-Me}_2\text{C}_6\text{H}_3\text{NHCSSEt}$, m. 65° .²¹⁵
p- $\text{MeOC}_6\text{H}_4\text{NHCSSMe}$, m. 101° .²¹⁵
p- $\text{MeOC}_6\text{H}_4\text{NHCSSEt}$, m. 77° .²¹⁵
 $\text{EtOC}_6\text{H}_4\text{NHCSSMe}$, *o*, m. 52° ; *p*, m. 104° .²¹⁵
 $\text{EtOC}_6\text{H}_4\text{NHCSSEt}$, *o*, m. 79° ; *p*, m. 93° .²¹⁵
 $\text{BrC}_6\text{H}_4\text{NHCSSMe}$, *o*, m. 120° ; *p*, m. 69° .²¹⁵
p- $\text{H}_2\text{NC}_6\text{H}_4\text{NHCSSMe}$, m. 140° .⁵¹⁸
m- $\text{EtOCC}_6\text{H}_4\text{NHCSSMe}$, m. 73° .²¹⁵
m- $\text{EtOCC}_6\text{H}_4\text{NHCSSEt}$, m. 67° .²¹⁵
p- $\text{HOCC}_6\text{H}_4\text{NHCSSC}_6\text{H}_4\text{Me}$ -*p*, Me ester, m. 174° ; Et ester, m. 167° ; *i*-Pr ester, m. 141° ; Bu ester, m. 130° ; *i*-Am ester, m. 126° ; allyl ester, m. 143° .²¹⁰
 $\text{C}_{10}\text{H}_7\text{NHCSSMe}$, m. 117° .¹³⁹⁸
 $\text{C}_{10}\text{H}_7\text{NHCSSCH}_2\text{COOEt}$, α m. 81° ; β m. 83° .¹⁶⁷⁰

DISUBSTITUTED DITHIOCARBAMATES

 Me_2NCSSR

- Methyl-, m. 47° ; ^{171b}, ^{408b}, ^{412c}, ^{415a} b. 243° ; ^{408b}, ^{412c}, ^{414b}, ^{415a}, ^{415b} d 18/4 1.0861; n 18.5/D 1.58118; ^{415b} ultra violet absorption.⁸
Ethyl-, m. 2° ; ^{415a}, ¹⁶¹⁹ b. 252° ; ^{408b}, ^{412c}, ^{415a}, ¹⁶¹⁹ d 0/4 1.1255, ^{408b}, ^{412c}, ^{415a} 1.12581, ^{415a} d 15/4 1.114, d 18/4 1.1112, ^{415b} d 18.5/4 1.1108, ^{415a} d 19/4 1.1104; ^{415b} n 18/D 1.59588, n 19/D 1.57526; ^{415b} dipole moment, 3.22.⁶⁹⁰
Butyl-, ^b₂₀ $157\text{--}9^\circ$; ³⁹⁶ ^b₂₅ $170\text{--}5^\circ$.²⁴²
Hexyl-, ^b₁₀ 168° .⁹⁶⁶
Dodecyl-, m. 40° .⁹⁶⁶
Cetyl-, m. 49° .⁹⁶⁶
Allyl-, m. 2° ; ^{408b} ^b₂₀ 140° , ³⁹⁶ b. 252° ; d 0/4 1.12581, d 18.5/4 1.1108.^{408b}
 $\text{BuOCH}_2\text{-}$, ^b₂ 137° ; d 25/4 1.0791; n 25/D 1.5551.^{812c}

HOCH₂CH₂-, b. 162°; *p*-nitrobenzoate, m. 141°; monosuccinate, m. 80°; monophthalate, m. 109°; PhNHCOOCH₂CH₂-, m. 103°. ^{1204b}

HSCH₂CH₂-, m. 86°. ⁴⁰⁵

CH₂:CClCH₂-, m. 37°; ^{728, 729} b₁ 126–8°. ⁷²⁹

ClCH:CHCH₂-, n 25/D 1.6135. ⁷²⁸

MeClC:CHCH₂-, m. 28°. ^{728, 729}

MeCOCH₂-, m. 73°. ^{1204b} 58°. ¹³⁷²

NCCH₂-, m. 73°. ^{1204b}

NCCH₂CH₂-, m. 38°. ^{404a}

HOOCCH₂-, m. 148°, ^{146a} 144°; ^{861b} amide, m. 125°; ^{1204b} 122°; ^{1016b, 1017a} Me amide, m. 115°; PhCH₂ amide, m. 112°; Me ester, m. 48°; ^{1204b} Et ester, m. 64°, ^{146a} 60°; Pr. ester, m. 44°. ^{1204b}

H₂NNHCOCH₂-, m. 134°; Me₂C:NNHCOCH₂-, m. 160°; PhCH₂C(COOH):NNHCOCH₂-, m. 160°. ^{1204b}

PhNHNHCOCH₂-, m. 95°. ^{1204b}

HOOCCHMe-, m. 135°; amide, m. 127°; Me amide, m. 95°; Me ester, m. 38.5°; Et ester, m. 59.5°. ^{1204b}

HOCCMe₂-, m. 137°; amide, m. 69°; Me amide, m. 61°. ^{1204b}

HOOCCH₂CH₂-, m. 143°, ⁶⁶⁷ 140.5°; amide, m. 121°. ^{404a}

EtOOCCH(COMe)-, m. 68°. ¹⁷⁷⁹

2-Benzothiazolyl-, m. 123°. ¹³⁶³

2-Benzoquinonyl SCH₂CH₂-, m. 133°. ¹⁶⁸²

2-(1,4-Naphthoquinonyl) SCH₂CH₂-, m. 209°. ¹⁶⁸²

PhNHCH₂-, m. 83°. ^{723b}

Me₂NCH₂-, m. 39°. ⁵³¹

Ph₂NCH₂-, m. 93°. ^{723b}

Ph(α-C₁₀H₇)NCH₂-, m. 174°. ^{723b}

Me₂NCH₂CH₂-, m. 38°; ^{303a, 1538} b₁₅ 170–6°; ¹⁵³⁸ HCl, m. 181°, ^{303a} 180°, ¹⁵³⁸ 139°; ³⁸⁶ MeCl, m. 198°; MeI, m. 197°; Me₂SO₆, m. 100°; C₁₂H₂₅Br, m. 122°. ¹⁵³⁸

Et₂NCH₂CH₂-, HCl, m. 145°. ³⁸⁶

PhN:CHCH₂-, m. 72°. ^{1121b}

HN:C(OEt)CH₂-, m. 58°; HCl, m. 140°. ^{1204b}

HON:C(NH₂)CH₂-, m. 162°; *p*-nitrobenzoate, m. 195°. ^{1204b}

H₂NN:CMech₂-, m. 127°. ^{1204b}

HON:CMech₂-, m. 101°; Ac., m. 191°; Bz., m. 167°. ^{1204b}

2,4-(O₂N)₂C₆H₃NHN:CMech₂-, m. 146°. ^{1204b}

H₂NCONHN:CMech₂-, m. 217° dec. ^{1204b}

- $\text{H}_2\text{NCSNHN:CMeCH}_2^-$, m. 176° .^{1204b}
 $\text{HON:C(NHCONHPh)CH}_2^-$, m. 139° .^{1204b}
 $\text{H}_2\text{N(HON:)}\text{CCH}_2\text{CH}_2^-$, m. 131° .^{404a}
 $\text{H}_2\text{N(HN:)}\text{CCH}_2\text{CH}_2^-$, picrate, m. 208° .^{404a}
 9-Acridyl-, m. 230° .²⁸⁵
 2-Me-9-acridyl-, m. 217° .²⁸⁵
 2-MeO-9-acridyl-, m. 190.5° .²⁸⁵
 2-Cl-2-MeO-9-acridyl-, m. 190° .²⁸⁵
 3-Cl-9-acridyl-, m. 204° .²⁸⁵
 Phenyl-, m. 75.5° .³¹⁵
 Benzyl-, m. 41° ; ^{396, 966} b_{20} 220° .³⁹⁶
 Tolyl-, *o*, m. 82° ; *p*, m. 113° .³¹⁵
 $\text{PhCH}_2\text{CH}_2^-$, m. 46° .⁹⁶⁶
 $p\text{-O}_2\text{NC}_6\text{H}_4^-$, m. 157° ,⁹⁶⁶ 154° .³¹⁵
 $2,4\text{-(O}_2\text{N)}_2\text{C}_6\text{H}_3^-$, m. 153° ; ⁹⁶⁶ dipole moment, 6.31.⁶⁹⁰
 $p\text{-BrC}_6\text{H}_4^-$, m. 121° .³¹⁵
 $2,4\text{-Me}_2\text{C}_6\text{H}_3\text{CH}_2^-$, b_{10} $219\text{--}22^\circ$.⁹⁶⁶
 $p\text{-O}_2\text{NC}_6\text{H}_4\text{CH}_2^-$, m. 107° .⁹⁶⁶
 $p\text{-ClC}_6\text{H}_4\text{CH}_2^-$, m. 55° .⁹⁶⁶
 $\text{Cl}_2\text{C}_6\text{H}_3\text{CH}_2^-$, 2,4-, m. 83° ; 3,4-, m. 76° .⁹⁶⁶
 $3,4\text{-O}_2\text{N(MeO)C}_6\text{H}_3\text{CH}_2^-$, m. 103° .⁹⁶⁶
 $p\text{-MeC}_6\text{H}_4\text{OCH}_2\text{CH}_2^-$, m. 65° .⁹⁶⁶
 $p\text{-Me}_3\text{CC}_6\text{H}_4\text{OCH}_2\text{CH}_2^-$, m. 62° .⁹⁶⁶
 $4,2\text{-Me(Me}_3\text{C)C}_6\text{H}_3\text{OCH}_2\text{CH}_2^-$, m. 79° .⁹⁶⁶
 $p\text{-ClC}_6\text{H}_4\text{OCH}_2\text{CH}_2^-$, m. 74° .⁹⁶⁶
 $2,4\text{-Cl}_2\text{C}_6\text{H}_3\text{OCH}_2\text{CH}_2^-$, m. 74° .⁹⁶⁶
 $p\text{-ClC}_6\text{H}_4\text{O(CH}_2)_3^-$, m. 93° .⁹⁶⁶
 $p\text{-ClC}_6\text{H}_4\text{O(CH}_2)_4^-$, m. 65° .⁹⁶⁶
 $p\text{-ClC}_6\text{H}_4\text{SCH}_2\text{CH}_2^-$, m. 97° .⁹⁶⁶
 $p\text{-ClC}_6\text{H}_4\text{CH}_2\text{SCH}_2\text{CH}_2^-$, m. 51° .⁹⁶⁶
 $2,4\text{-O}_2\text{N(OCH)C}_6\text{H}_3^-$, m. 132° .⁸²⁷
 $\text{O}_2\text{N(HOOC)C}_6\text{H}_3^-$, 2,4-, amide, m. 198° ; Me ester, m. 130° ;
 4,2-, *c*-Hexyl ester, m. 113° .⁸²⁷

Bis-DITHIOCARBAMATES

- $\text{CH}_2(\text{SCSNMe}_2)_2$, m. 153° .¹⁶⁰⁷
 $(\text{CH}_2\text{SCSNMe}_2)_2$, m. 189° .²⁴²
 $\text{CO(CH}_2\text{SCSNMe}_2)_2$, m. 158° .¹³⁷²
 $\text{MeCOCH(CH}_2\text{SCSNMe}_2)_2$, m. 101° .^{146a}
 $\text{PhCOCH(CH}_2\text{SCSNMe}_2)_2$, m. 141° .^{146a}

$\text{CO}[\text{CH}(\text{CH}_2\text{SCSNMe}_2)_2]_2$, m. 147° .^{146a}
 $\text{EtOOCCH}(\text{SCSNMe}_2)_2$, m. 178° .^{1016a}
 $\text{MeN}(\text{CH}_2\text{CH}_2\text{SCSNMe}_2)_2$, m. 60° ; HCl , m. 165° ; MeI , m. 161° ;
 Me_2SO_4 , m. 131° .¹⁵³⁸
 $\text{Me}_2\text{NCSSCH}_2\text{C}(\text{NMe}_2):\text{CHSCSNMe}_2$, m. 103° .¹³⁷²
 $4,2\text{-Me}(\text{Me}_2\text{NCSSCH}_2)\text{C}_6\text{H}_3\text{OCH}_2\text{CH}_2\text{SCSNMe}_2$, m. 115° .⁹⁶⁶
 $\text{S}(\text{CH}_2\text{CH}_2\text{SCSNMe}_2)_2$, m. 112° .⁹⁶⁶
 $p\text{-C}_6\text{H}_4(\text{CH}_2\text{SCSNMe}_2)_2$, m. 179° .⁹⁶⁶

Et_2NCSSR

Methyl-, m. 2° ; ^{412c} b. 256° ; d 0/4 1.0977,^{408b, 412c, 415a} d 17/4
 1.0870,^{408b, 415a} d 18.5/4 1.0861; n 18.5/D 1.58118.^{415b}
 Allyl-, b. 111° .^{1648a}
 Phenyl-, m. 46° .³¹⁵
 p -Tolyl-, m. 78° .³¹⁵
 $\text{Ph}_3\text{C-}$, m. 153° .^{226b}
 $\text{CH}_2:\text{CClCH}_2\text{-}$, b₁ $128\text{--}30^\circ$; ^{728, 729} n 25/D 1.5822.⁷²⁸
 $\text{ClCH:CHCH}_2\text{-}$, m. 25/D 1.5891.⁷²⁸
 $\text{ClMeCH:CHCH}_2\text{-}$, b₂ $158\text{--}60^\circ$; ^{728, 729} n 25/D 1.5800.⁷²⁸
 $\text{PhCOCH}_2\text{-}$, m. 104° .⁷⁶⁷
 $\text{NCCH}_2\text{CH}_2\text{-}$, oil.^{404a}
 $\text{H}_2\text{N}(\text{HN:})\text{CCH}_2\text{CH}_2\text{-}$, m. 189° .^{404a}
 $\text{H}_2\text{N}(\text{HON:})\text{CCH}_2\text{CH}_2\text{-}$, m. 59° .^{404a}
 $\text{HOOCCH}_2\text{-}$, m. 89° .^{861b}
 $\text{HOOCCH}_2\text{CH}_2\text{-}$, m. 98° ,⁶⁶⁷ 95° ,⁶⁶⁶ 91.5° ; amide, m. 106° ,^{404a}
 105° .²¹¹
 $\text{HOOCCH}_2\text{CH}(\text{COOH})\text{-}$, m. 107° ; $[\alpha]_D -6.67$.^{887b, 887c}
 $\text{H}_2\text{NCOCH}_2\text{CH}(\text{COOH})\text{-}$, L m. 128° ; $[\alpha]_D -18.8$; D m. 145° ;
 $[\alpha]_D 74.3$; L Et ester, m. 86° .^{887b}
 $\text{HOOCCH}_2\text{CH}(\text{COOEt})\text{-}$, L m. 111° ; amide, m. 86° .^{887b}
 $\text{Me}_2\text{NCH}_2\text{CH}_2\text{-}$, b₁₆ $180\text{--}5^\circ$; ¹⁵³⁸ HCl , m. 133° .³⁸⁶
 $\text{Et}_2\text{NCH}_2\text{CH}_2\text{-}$, b₁₂ 180° ; ¹⁵³⁸ HCl , m. 107° ,³⁸⁶ 105° .¹⁵³⁸
 $\text{Me}_2\text{NCH}_2\text{CHMe}$, HCl , m. 133° .³⁸⁶
 $\text{HSCH}_2\text{CH}_2\text{-}$, m. 90° .⁴⁰⁵
 $\text{ClCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{-}$, m. 40.5° .¹²⁷⁹
 $\text{S}(\text{CH}_2\text{CH}_2\text{SCSNEt}_2)_2$, m. 66° .¹²⁷⁹
 2-Benzothiazolyl- , m. 79.5° ,¹⁰⁰⁹ 79° .¹³⁶³
 $4,5\text{-Dihydronaphtho}[1,2]\text{-thiazol-2-yl-}$, m. 118° .³⁸⁵

Pr_2NCSSR

Methyl-, m. 0° ; b. 275° ,^{408b, 412c, 415a} b_{77} 193° ; ^{408b, 415a} d 0/4 1.0475,^{408b, 412c, 415a} d 13/4 1.0377,^{408b, 415a} d 18/4 1.0340; n 18/D 1.56087.^{415b}
 Ethyl-, b_{28} $170-2^\circ$.^{171b}
 Propyl-, b_{10} 160° .^{171b}
 $p\text{-O}_2\text{NC}_6\text{H}_4\text{CH}_2\text{-}$, m. 60° .^{412c}

 Bu_2NCSSR

Ethyl-, dipole moment, 3.25.⁶⁹⁰
 Butyl-, b_1 163° .²⁴²
 Vinyl-, b_5 148° ; n 25/D 1.5543.⁷¹⁵
 $\text{HOOCCH}_2\text{-}$, m. 69° .^{861b}
 $\text{H}_2\text{NCOCH}_2\text{CH}_2\text{-}$, m. 62° .²¹¹
 $\text{Me}_2\text{NCH}_2\text{CH}_2\text{-}$, $b_{0.2}$ 163° ; ^{1541c} HCl, m. 93° .^{386, 1541c}
 $\text{Et}_2\text{NCH}_2\text{CH}_2\text{-}$, $b_{0.2}$ $167-9^\circ$; ^{1541c} HCl, m. 92° .^{386, 1541c}
 $\text{Me}_2\text{NCH}_2\text{CHMe-}$, $b_{0.2}$ $162-4^\circ$; ^{1541c} HCl, m. 93° .^{386, 1541c}

HIGHER DIALKYLDITHIOCARBAMATES

Am_2NCSSAm , b_{17} $160-80^\circ$.²⁴²
 $\text{Allyl}_2\text{NCSSCH}_2\text{CCl:CH}_2$, b_1 146° ; ^{728, 729} n 25/D 1.5881.⁷²⁸

 $(\text{CH}_2)_5\text{NCSSR}$

Methyl-, m. 34° ,^{412c} 32° ; b_{16} $164-6^\circ$.³⁹⁶
 Vinyl-, b_8 151° ; n 25/D 1.5978.⁷¹⁵
 $\text{HOCH}_2\text{CH}_2\text{-}$, m. 18° ; p -nitrobenzoate, m. 91° ; monophthalate, m. 125° ; monosuccinate, m. 56° ; $\text{PhNHCOOCH}_2\text{CH}_2\text{-}$, m. 92° .^{1204b}
 $\text{HSCH}_2\text{CH}_2\text{-}$, m. 111° .⁴⁰⁵
 $\text{MeCOCH}_2\text{-}$, m. 62° ; oxime, m. 110° ; hydrazone, m. 84° ; 2,4-dinitrophenylhydrazone, m. 135° ; semicarbazone, m. 183° ; thiosemicarbazone, m. 175° .^{1204b}
 $\text{Me}_2\text{NCH}_2\text{CH}_2\text{-}$, EtI, m. 140.5° ; Et_2SO_4 , m. 76° ; ()₂ Et_2SO_4 , m. 117° .^{1696a}
 $\text{NCCH}_2\text{-}$, m. 74° .^{1204b}
 $\text{NCCH}_2\text{CH}_2\text{-}$, m. 79.5° .^{404a}
 $\text{HN:C(OEt)CH}_2\text{-}$, m. 54° ; HCl, m. 190° .^{1204b}
 $\text{HON:C(NH}_2\text{)CH}_2\text{-}$, m. 77° .^{1204b}
 $\text{HN:C(NH}_2\text{)CH}_2\text{CH}_2\text{-}$, HI, m. 162.5° .^{404a}

- $\text{HON:C(NH}_2\text{)CH}_2\text{CH}_2\text{-}$, m. 122° .^{404a}
 $\text{HOOCCH}_2\text{-}$, m. 143° ; ^{1204b} amide, m. 145° ,^{1017a} 144.5° ,^{1016b}
 143° ; ^{1204b} anilide, m. 121° ; ^{1016b} Me ester, m. 59.5° ; Et ester,
m. 68° .^{1204b}
 $\text{H}_2\text{NNHCOCH}_2\text{-}$, m. 141° .^{1204b}
 $\text{PhNHNHCOCH}_2\text{-}$, m. 185° .^{1204b}
 $\text{HOOCCH}_2\text{CH}_2\text{-}$, m. 104° ; amide, m. 116° ,^{404a} 115° .²¹¹
Phenyl-, m. 78° .³¹⁵

-Tolyl-, m. 90.4° .³¹⁵
 $2,4\text{-O}_2\text{N(HOOC)C}_6\text{H}_3\text{-}$, m. 89° .⁸²⁷
Benzoquinone $\text{SCH}_2\text{CH}_2\text{-}$, m. 123° .¹⁶⁸²
1,4-Naphthoquinone $\text{SCH}_2\text{CH}_2\text{-}$, m. 163° .¹⁶⁸²
 $\text{CH}_2[\text{CH}_2\text{SCSN(CH}_2\text{)}_5]_2$, m. 140° .^{173a}
 $[\cdot\text{CH}_2\text{CH}_2\text{SCSN(CH}_2\text{)}_5]_2$, m. 125° .^{173a}
 $\text{CH}_2[\text{CH}_2\text{CH}_2\text{SCSN(CH}_2\text{)}_5]_2$, m. 103° .^{173a}
 $[\cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{SCSN(CH}_2\text{)}_5]_2$, m. 94° .^{173a}
 $[\cdot\text{CH}_2(\text{CH}_2)_4\text{SCSN(CH}_2\text{)}_5]_2$, m. 90° .^{173a}

DITHIOCARBAMATES OF OTHER CYCLIC AMINES

- Pyridyl CSSMe, 2-, m. 89° ; 3-, m. 135° .⁵¹⁸
Quinolyl CSSMe, 5-, m. 148° ; 6-, m. 161° ; 8-, m. 101° .⁵¹⁸
4-IsoquinolylCSSMe, m. 140° .⁵¹⁸

$\text{O(CH}_2\text{CH}_2)_2\text{NCSSR}$

- Vinyl-, b_{18} 93° ; n 25/D 1.5296.⁷¹⁵
 $\text{ClCH:CHCH}_2\text{-}$, m. -10° ; ^{728, 729} n 25/D 1.6261.⁷²⁸
 $\text{MeClCH:CHCH}_2\text{-}$, m. 57° .^{728, 729}
 $\text{HOCH}_2\text{CH}_2\text{-}$, m. 47° ; *p*-nitrobenzoate, m. 117° ; monosuccinate,
m. 97° ; monomaleate, m. 100° ; monophthalate, m. 128° ;
 $\text{PhNHCOOCH}_2\text{CH}_2\text{-}$, m. 152° .^{1204b}
 $\text{HSCH}_2\text{CH}_2\text{-}$, m. 103° .⁴⁰⁵
 $\text{Me}_2\text{NCH}_2\text{CH}_2\text{-}$, EtI, m. 124° ; Et_2SO_4 , m. 68° ; ()₂ Et_2SO_4 , m.
 117° .^{1696a}
 $\text{MeCOCH}_2\text{-}$, m. 94° ; hydrazone, m. 98° ; 2,4-dinitrophenylhy-
drazone, m. 147° ; oxime, m. 102° ; semicarbazone, m. 186° ;
thiosemicarbazone, m. 186° .^{1204b}
 $\text{NCCH}_2\text{-}$, m. 103° .^{1204b}
 $\text{NCCH}_2\text{CH}_2\text{-}$, m. 86.5° .^{404a}
 $\text{HON:(H}_2\text{N)CCH}_2\text{-}$, m. 156° .^{1204b}

NH:(EtO)CCH₂-, m. 79°; HCl, m. 139°. ^{1204b}
 HON:(H₂N)CCH₂CH₂-, m. 144°. ^{404a}
 NH:(H₂N)CCH₂CH₂-, picrate, m. 194°. ^{404a}
 HOOCCH₂-, m. 162°; amide, m. 155°, ^{1204b} 146°; ²¹¹ Me ester, m. 57°; Et ester, m. 70°. ^{1204b}
 H₂NNHCOCH₂-, m. 133°. ^{1204b}
 PhNHNHCOCH₂-, m. 84°. ^{1204b}
 HOOCCH₂CH₂-, m. 123.5°; ^{404a} amide, m. 146°, ²¹¹ 138.5°. ^{404a}
 2-Benzoquinone SCH₂CH₂-, m. 138°. ¹⁶⁸²
 2-(1,4-Naphthoquinone) SCH₂CH₂-, m. 174°. ¹⁶⁸²

HN(CH₂CH₂)₂NCSSR

Benzyl-, oil; HCl, m. 176°. ³⁸⁷
 PhCH₂N(CH₂CH₂)₂NCSSCH₂Ph, m. 68°. ³⁸⁷
 PhCH₂SCSN(CH₂CH₂)₂NCSSCH₂Ph, m. 124.5°. ³⁸⁷
 NCCH₂CH₂SCSN(CH₂CH₂)₂NCSSCH₂CH₂CN, m. 140°. ^{404b}
 HOOCCH₂CH₂SCSN(CH₂CH₂)₂NCSSCH₂CH₂COOH, m. 196°; ⁴ amide, m. 231.5°. ^{404b}
 CH₂:CClCH₂SCSN(CHMeCH₂)₂NCSSCH₂CCl:CH₂, m. 125°, ⁷²⁸, ⁷²⁹
 ClMeC:CHCH₂SCSN(CHMeCH₂)₂NCSSCH₂CH:CMcCl, m. 103°. ⁷²⁸, ⁷²⁹

AMINOALKYLDITHIOCARBAMATES

Me₂NCH₂CH₂(Me)NCSSMe, HCl, m. 181°. ³⁸⁶
 Et₂NCH₂CH₂(Me)NCSSMe, HCl, m. 180.5°. ³⁸⁶
 Et₂NCH₂CH₂(Me)NCSSEt, HCl, m. 146°. ³⁸⁶
 Et₂NCH₂CH₂(Me)NCSS Allyl, HCl, m. 139°. ³⁸⁶
 Et₂NCH₂CH₂(Et)NCSSMe, HCl, m. 96.5°. ³⁸⁶
 Et₂NCH₂CH₂(Et)NCSSC₁₀H₂₁, b_{0.2} 198–202°; ^{1541b} HCl, m. 94°. ³⁸⁶, ^{1541b}
 Et₂NCH₂CH₂(Et)NCSSCH₂CH₂NMe₂, HCl, m. 165.6°. ³⁸⁶
 Et₂NCH₂CH₂(Et)NCSSCH₂CH₂NEt₂, HCl, m. 146°. ³⁸⁶
 Et₂NCH₂CH₂(Et)NCSSCH₂COOEt, HCl, m. 120°. ³⁸⁶
 Et₂NCH₂CH₂(Et)NCSSCH₂Ph, b₁₁ 234–8°; ^{1541b} HCl, m. 106°. ³⁸⁶, ^{1541b}
 Et₂NCH₂CH₂(i-Pr)NCSS Allyl, HCl, m. 56°. ³⁸⁶
 Et₂NCH₂CH₂CH₂CHMe(Et)NCSSMe, b₁₇ 197°. ³⁸⁶
 Et₂NCH₂CH₂CH₂CHMe(Et)NCSSC₇H₁₅, b₁₂ 241°. ³⁸⁶

$\text{Et}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{CHMe}(\text{Et})\text{NCSSCH}_2\text{C}_6\text{H}_3(\text{OMe})_{2-3,4}$, b_{12}
278–80°. ³⁸⁶

$\text{Et}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{CHMe}(\text{PhCH}_2)\text{NCSSMe}$, $b_{0.4}$ 210°. ³⁸⁶

Bis-Amino Bis-Dithiocarbamates ^{404b}

$(\cdot\text{CH}_2\text{NMeCSSCH}_2\text{CH}_2\text{CN})_2$, m. 151°.
 $(\cdot\text{CH}_2\text{NMeCSSCH}_2\text{CH}_2\text{COOH})_2$, m. 243°; amide, m. 233.5°.
 $(\cdot\text{CH}_2\text{NEtCSSCH}_2\text{CH}_2\text{CN})_2$, m. 102°.
 $(\cdot\text{CH}_2\text{NEtCSSCH}_2\text{CH}_2\text{COOH})_2$, m. 174°; amide, m. 191°.
 $(\cdot\text{CH}_2\text{NCH}_2\text{PhCSSCH}_2\text{CH}_2\text{CN})_2$, m. 119.5°.
 $(\cdot\text{CH}_2\text{NCH}_2\text{PhCSSCH}_2\text{CH}_2\text{COOH})_2$, m. 187°; amide, m. 131°.
 $\text{CH}_2(\text{CH}_2\text{NMeCSSCH}_2\text{CH}_2\text{CN})_2$, m. 93°.
 $\text{CH}_2(\text{CH}_2\text{NMeCSSCH}_2\text{CH}_2\text{COOH})_2$, m. 132.5°; amide, m. 152°.
 $\text{CH}_2(\text{CH}_2\text{NEtCSSCH}_2\text{CH}_2\text{CN})_2$, m. 56°.
 $\text{CH}_2(\text{CH}_2\text{NEtCSSCH}_2\text{CH}_2\text{COOH})_2$, m. 96°; amide, m. 199°.
 $(\cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{NMeCH}_2\text{CH}_2\text{CN})_2$, m. 72.5°.
 $(\cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{NMeCH}_2\text{CH}_2\text{COOH})_2$, m. 103.5°; amide, m. 141°.
 $(\cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{NEtCH}_2\text{CH}_2\text{CN})_2$, m. 93.5°.
 $(\cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{NEtCH}_2\text{CH}_2\text{COOH})_2$, m. 87°; amide, m. 145.5°.

Me(Ph)NCSSR

Methyl-, m. 88°, ¹⁰⁸ 81.5°; b_1 311°; ^{408c} ultraviolet absorption.⁸
 Ethyl-, m. 95.5°. ⁷⁴⁵
 $\text{H}_2\text{NCOCH}_2\text{CH}_2-$, m. 125°. ²¹¹
 Phenyl-, m. 99.5°. ^{1365b}

Et(Ph)NCSSR

Methyl-, m. 53°. ⁷⁴⁵
 Ethyl-, m. 68°, ¹⁰⁵ 66.4°. ¹²¹
 $\text{H}_2\text{NCOCH}_2\text{CH}_2-$, m. 96°. ²¹¹
 Phenyl-, m. 128°, ¹²¹ 127.8°. ^{1365b}
 2-Benzothiazolyl-, m. 105–8°. ¹³⁶³

Ar₂NCSSR

$\text{Me}(p\text{-MeC}_6\text{H}_4)\text{NCSSMe}$, m. 82°. ²¹⁵
 $\text{Me}(p\text{-MeC}_6\text{H}_4)\text{NCSSEt}$, m. 84°. ²¹⁵
 Ph_2NCSSEt , dipole moment, 3.12. ⁶⁹⁰
 $\text{Ph}_2\text{NCSSCH}_2\text{CH}_2\text{SH}$, m. 139°. ⁴⁰⁵
 $\text{Ph}(\text{PhCH}_2)\text{NCSSEt}$, m. 76°. ²¹⁵
 $(\text{PhCH}_2)_2\text{NCSSMe}$, m. 55°. ^{412c}

$(\text{PhCH}_2)_2\text{NCSSCH}_2\text{CH}_2\text{CONH}_2$, m. 105° .²¹¹

$\text{PhCOCH}[\text{N}(\text{CH}_2\text{Ph})\text{CS}_2\text{CH}_2\text{COMe}]\text{CH}_2\text{COOH}$, m. 131° .^{267d}

IMINOTHIOCARBONIC

$\text{MeSC}(\text{OMe})\text{:NH}$, HCl, dec. 62° .^{947a}

$\text{MeSC}(\text{OEt})\text{:NH}$, HCl, dec. 85° ; ^{947a} HI, m. 60° .^{947c}

$\text{EtSC}(\text{OMe})\text{:NH}$, HCl, dec. 49° .^{947a}

$\text{EtSC}(\text{OEt})\text{:NH}$, HCl, dec. 75° .^{947a}

$\text{PhSC}(\text{OEt})\text{:NH}$, HCl, dec. 75° .^{947a}

Allyl $\text{N:C}(\text{SAg})\text{OMe}$, m. 157° .¹⁴⁵⁴

Allyl $\text{N:C}(\text{SAg})\text{OEt}$, m. $112-8^\circ$,¹⁴⁵² 170° .¹⁴⁵⁶

Allyl $\text{N:C}(\text{SAg})\text{OPr}$, m. 135° .¹⁴⁵⁴

Allyl $\text{N:C}(\text{SAg})\text{OPh}$, m. $<140^\circ$.¹⁴⁵⁷

$\text{MeSO}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{N:C}(\text{SAg})\text{OMe}$, m. 141° .¹⁴⁵⁴

$\text{MeSO}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{N:C}(\text{SAg})\text{OEt}$, m. 150° .¹⁴⁵⁴

$\text{PhN:C}(\text{SAg})\text{OPh}$, m. 186° .¹⁴⁵⁷

$\text{MeN:C}(\text{SMe})\text{OMe}$, b. 143° ,^{415b} $142-4^\circ$; ^{410b} d 0/4 1.0654,^{410b} d 0/4 1.065,^{415b} d 19/4 1.0457,^{410b} d 20/4 1.0446; n 20/D 1.48548; ^{410b}, ^{415b} picrate, m. 110° .^{410b}

$\text{MeN:C}(\text{SEt})\text{OMe}$, b. $158-60^\circ$; d 0/4 1.0320, d 19/4 1.0125; n 20.5/D 1.48189; picrate, m. 100° .^{410b}

$\text{EtN:C}(\text{SMe})\text{OMe}$, b. 155° ; d 0/4 1.02545, d 19/4 1.0056,^{410b} d 20.5/4 1.0040; ^{415b} n 20.5/4 1.47888; ^{410b}, ^{415b} picrate, m. 94° .^{410b}

Allyl $\text{N:C}(\text{SMe})\text{OMe}$, b_{13} $70-5^\circ$.¹⁴⁵⁴

Allyl $\text{N:C}(\text{SMe})\text{OEt}$, b_{13} $76-80^\circ$.¹⁴⁵⁴

Allyl $\text{N:C}(\text{SEt})\text{OMe}$, b_{12} $76-80^\circ$.¹⁴⁵⁴

Allyl $\text{N:C}(\text{SEt})\text{OEt}$, b_{14} $88-92^\circ$.¹⁴⁵²

Allyl $\text{N:C}(\text{SPr})\text{OMe}$, b_{14} $91-5^\circ$.¹⁴⁵⁴

Allyl $\text{N:C}(\text{SPr})\text{OEt}$, b_{15} $101-5^\circ$.¹⁴⁵⁴

Allyl $\text{N:C}(\text{SPr})\text{OPr}$, b_{13} $111-5^\circ$.¹⁴⁵⁴

Allyl $\text{N:C}(\text{S Allyl})\text{OPr}$, b_{12} $112-6^\circ$.¹⁴⁵⁴

Allyl $\text{N:C}(\text{SEt})\text{OPh}$, b_{20} $150-60^\circ$.¹⁴⁵⁷

Allyl $\text{N:C}(\text{S-tetraacetyl glucoside})\text{OEt}$, m. 99° ; $[\alpha]_D^{18} -17.92$.¹⁴⁵⁴

$\text{MeSO}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{N:C}(\text{SEt})\text{OEt}$, m. 43° .¹⁴⁵⁴

$\text{MeSO}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{N:C}(\text{S-tetraacetylglucoside})\text{OEt}$, m. 113° ; ¹⁴⁵⁴, ¹⁴⁵⁷ $[\alpha]_D^{20} -4.66^\circ$ (in $(\text{CHCl}_2)_2$).¹⁴⁵⁴

2,4,6- $(\text{O}_2\text{N})_3\text{C}_6\text{H}_2\text{N:C}(\text{OMe})\text{SC}_6\text{H}_2(\text{NO}_2)_3$ -2,4,6, m. 169° .³⁵⁸

2,4,6- $(\text{O}_2\text{N})_3\text{C}_6\text{H}_2\text{N:C}(\text{OEt})\text{SC}_6\text{H}_2(\text{NO}_2)_3$ -2,4,6, m. 138° .³⁵⁸

2,4,6- $(\text{O}_2\text{N})_3\text{C}_6\text{H}_2\text{N:C}(\text{OPr})\text{SC}_6\text{H}_2(\text{NO}_2)_3$ -2,4,6, m. 152° .³⁵⁸

2,4,6- $(\text{O}_2\text{N})_3\text{C}_6\text{H}_2\text{N:C}(\text{OCHMe}_2)\text{SC}_6\text{H}_2(\text{NO}_2)_3$ -2,4,6, m. 147° .³⁵⁷

2,4,6-(O₂N)₃C₆H₂N:C(OCH₂CHMe₂)SC₆H₂(NO₂)₃-2,4,6, m. 173°. ³⁵⁶

2,4,6-(O₂N)₃C₆H₂N:C(OAm)SC₆H₂(NO₂)₃-2,4,6, m. 138.5°. ³⁵⁷

Tetraacetylphenylthiourethanglucoside, m. 159°; [α]_D¹⁵ -2.46. ¹⁴⁵³

(MeS)₂C:NH, d₀ 1.18; HI, m. 130°; ^{408d}, ^{415a} Ac., b₂₀ 142-4°. ^{1714c}

(EtS)₂C:NH, HI, m. 80-90°; ^{408d}, ^{415a} Ac., b₁₄ 142°. ^{1715a}

(i-AmS)₂C:NH, Ac., b₂₀ 198-200°. ^{1714c}

$$\begin{array}{c} \text{CH}_2\text{-S} \\ | \\ \text{CH}_2\text{S} \end{array} \text{C:NH, Ac., m. 69°; Bz., m. 143°; }^{1163} \text{HCl, m. 121°}.$$
 ^{1483b}

$$\begin{array}{c} \text{CH}_2\text{S} \\ | \\ \text{CH}_2\text{S} \end{array} \text{C:NOH, m. 126°}.$$
 ¹¹⁶³

$$\begin{array}{c} \text{Me-CHS} \\ | \\ \text{CH}_2\text{S} \end{array} \text{C:NH, HCl, m. 172-5°}.$$
 ¹¹⁶³

MeN:C(SMe)₂, b. 192°; ^{407a}, ^{407d}, ^{408b}, ^{412b}, ^{412c}, ^{414b}, ^{415a}, ^{415b} d 0/4 1.13827, ^{407d}, ^{408b}, ^{412b}, ^{415a} 1.138, ^{415b} 1.1383, ^{412c} d 11/4 1.1279, ^{415b} 1.12831, ^{415a} d 15/4 1.1248; n 11/D 1.56739; n 15/D 1.56460; ^{415b} PtCl₄, m. 180°; ^{171b}, ^{412b} ultraviolet absorption. ⁸

MeN:C(SMe)(SEt), b. 205-7°; d 0/4 1.0905, ^{408b}, ^{415a} d 13/4 1.0798, ^{415b} d 20/4 1.0741; ^{408b}, ^{415a} n 13/D 1.55166; ^{415b} HI, m. 77°; picrate, m. 103°; PtCl₄, m. 163°. ^{408b}

MeN:C(SEt)₂, b. 215°; ^{407d}, ^{408b}, ^{412b}, ^{412c}, ^{415a} d 0/4 1.0594, ^{407d}, ^{412b}, ^{415a} d 12/4 1.0489, ^{408b}, ^{412c}, ^{415a}, ^{415b} d 16.5/4 1.0436; n 12/D 1.53972, n 16.5/D 1.53650. ^{415b}

$$\begin{array}{c} \text{SCH}_2 \\ | \\ \text{MeN:C} \\ | \\ \text{SCH}_2 \end{array}, \text{ m. 184°}.$$
 ¹¹⁶³

EtN:C(SMe)₂, b. 201°; ^{407d}, ^{412b}, ^{415a} 200.5°; d 0/4 1.0848, ^{408b}, ^{412c} 1.08477, ^{407d}, ^{412b}, ^{415a} d 13.5/4 1.07195, ^{415b} d 18.4/4 1.0671; n 13.5/D 1.54837; ^{415b} PtCl₄, m. 150°. ^{412b}

EtN:C(SEt)₂, b. 223-4°; d 0/4 1.02905, ^{407d}, ^{412b}, ^{415a} d 13/4 1.0179, ^{415b} d 19.2/4 1.01248; ^{415a} n 13/D 1.53011; ^{415b} PtCl₄, m. 133°. ^{412b}

PrN:C(SMe)₂, b. 220-2°, ^{407d} 219°; d 0/4 1.0597, ^{412b}, ^{415a} 1.10093, ^{407d} d 12/4 1.0489, ^{415b} d 16.5/4 1.0451; ^{415a} n 12/D 1.53806; ^{415b} PtCl₄, m. 151°. ^{412b}

PrN:C(SEt)₂, b. 219°; d 0/4 1.0597, ^{407d} d 16.5/4 1.0451. ^{415a}

$\text{Me}_2\text{CHCH}_2\text{N}:\text{C}(\text{SMe})_2$, b. 225° ; d 0/4 1.0262,^{407d, 412b, 415a} d 15/4 1.0117,^{415b} d 16/4 1.0126; ^{415a} n 15/D 1.52570; ^{415b} PtCl_4 , m. 132° .^{412b}

$\text{Me}_2\text{CHCH}_2\text{CH}_2\text{N}:\text{C}(\text{SMe})_2$, b. 242° ,^{408b, 412c} $242\text{--}45^\circ$; ^{407b, 412b, 415a} d 0/4 1.0137,^{407b, 415a} 1.0262,^{412b, 412c} 1.0263,^{408b} d 16/4 1.0008; ^{415a, 415b} n 16/D 1.52271; ^{415b} PtCl_4 , m. 146° .^{412b}

$\text{Me}_2\text{CHCH}_2\text{CH}_2\text{N}:\text{C}(\text{SEt})_2$, b₇₇ 180° ,^{407d, 415a} b. 260° ; d 0/4 0.97906,^{407d, 412b, 415a} d 15.5/4 0.96642, d 18/4 0.9648; n 15.5/D 1.51303; ^{415a} PtCl_4 , m. 123° .^{412b}

Allyl $\text{N}:\text{C}(\text{SMe})_2$, b. $220\text{--}2^\circ$; d 0/4 1.10093,^{412b, 415a} d 18.5/4 1.0788,^{415b} d 21/4 1.08273; ^{415a} n 18.5/4 1.55940; ^{415b} 3 PtCl_4 , m. 145° .^{415b}

$\text{PhN}:\text{C}(\text{SMe})_2$, ultraviolet absorption.⁸

$\text{PhCH}_2\text{N}:\text{C}(\text{SMe})_2$, b₆₀ $210\text{--}20^\circ$; d 0/4 1.1610; ^{407d, 412b} PtCl_4 , m. 165° .^{412b}

$\text{MeC}_6\text{H}_4\text{N}:\text{C}(\text{SMe})_2$, d 15/4 1.1429; n 15/D 1.62963.⁴¹⁵

TRI- AND TETRATHIOCARBAMATES

$\text{Me}_2\text{NCS}\cdot\text{S}\cdot\text{SMe}$, b_{0.7} $104\text{--}8^\circ$.⁹³⁷

$\text{Me}_2\text{NCS}\cdot\text{S}\cdot\text{SCMe}_3$, m. $<0^\circ$; b₂ $170\text{--}5^\circ$.^{812b}

$(\text{CH}_2)_4\text{NCS}\cdot\text{S}\cdot\text{SSCMe}_3$, d 20/4 1.1330; n 20/D 1.5021.^{766b}

$(\text{CH}_2)_5\text{NCS}\cdot\text{S}\cdot\text{SSCMe}_3$, d 20/4 1.1531; n 20/D 1.6084.^{766b}

$\text{O}(\text{CH}_2\text{CH}_2)_2\text{NCS}\cdot\text{S}\cdot\text{SSCMe}_3$, d 20/4 1.1869; n 20/D 1.6018.^{766b}

$\text{PhCH}_2\text{CH}_2\text{CH}_2\text{NHCS}\cdot\text{S}\cdot\text{SSCMe}_3$, d 20/4 1.1031; n 20/D 1.5868.^{766b}

SULFENAMIDES

$\text{Me}_2\text{NCS}\cdot\text{SNH}_2$, Ac., m. 135° .¹⁵¹⁴

$\text{Et}_2\text{NCS}\cdot\text{SNH}_2$, Ac., m. 67° .¹⁵¹⁴

$\text{MePhNCS}\cdot\text{SNH}_2$, m. 87° ; Ac., m. 128° .¹⁵¹⁴

$\text{Ph}_2\text{NCS}\cdot\text{SNH}_2$, Ac., m. 167° .¹⁵¹⁴

$\text{CH}_2\text{SO}_2\text{CH}_2\text{CH}_2\text{CHNRC}\cdot\text{S}\cdot\text{SNH}_2$, Me, m. 145° ; Allyl, m. $80\text{--}6^\circ$.¹⁶⁰¹

THIOCARBAZATES

Thiolcarbazates

PhNHNHCOSMe , m. 152° .^{1712b}

PhNHNHCOSEt , m. 112° .^{1712b}

MeSCONHNHCOSMe , m. 173° .³⁸

Thioncarbazates

EtOCSNHNH₂, *b*_{0.2} 105–20°; *d* 15/4 1.191; HCl, *m.* 141°; sulfate, *m.* 158° dec.; Bz., *m.* 154°. ¹⁶⁷⁸
c-HexOCSNHNH₂, *m.* 77°; Ac., *m.* 140°; Bz., *m.* 122.5°. ¹¹
 PhCH₂OCSNHNH₂, *m.* 62°; HCl, *m.* 108° dec.; ¹⁶⁷⁸ Ac., *m.* 137.5°; Bz., *m.* 136°. ^{11, 1678}
 PhNHNHCSOMe, *m.* 111°. ^{213a}
 PhNHNHCSOEt, *m.* 74°, ⁶⁸² 70°. ¹⁶⁷⁸
 PhNHNHCSOC₈H₁₁, *m.* 119.5°. ¹¹
 PhNHNHCSOCH₂Ph, *m.* 136.5°. ¹⁶⁷⁸
 (EtOCSNH)₂, *m.* 62°. ¹⁶⁷⁸
 (*c*-HexOCSNH)₂, *m.* 95°. ¹¹
 (PhCH₂OCSNH)₂, *m.* 119.5°. ^{11, 1678}
 EtOCSNHNHCSOCH₂Ph, *m.* 88°. ¹⁶⁷⁸
 EtOCSNHNHCONH₂, *m.* 161°. ⁶⁸²
 EtOCSNHNHCSNH₂, *m.* 156°. ⁶⁸²

R:NNHCSOEt ¹⁶⁷⁸

H₂C:, *m.* 58°.
 MeCH:, *m.* 89.5°.
 Me₂C:, *m.* 61.5°.
 MeEtC:, *m.* 70°.
 PhCH:, *m.* 102°.
 MePhC:, *m.* 102.5°.
 Ph₂C:, *m.* 106.5°.
 (CH₂)₅:C:, *m.* 100.5°.
 HOCCMe:, *m.* 143°.
 HOCCCH₂CH₂CMe:, *m.* 136.5°.
 C₄H₉O·CH:, *m.* 129.5°.

PhCH:NNHCSOC₈H₁₁, *m.* 112°. ¹¹
 PhCH:NNHCSOCH₂Ph, *m.* 124.5°. ¹¹

R:NNHCSOPh ¹⁶⁷⁸

MeCH:, *m.* 113.5°.
 Me₂C:, *m.* 68°.
 MeEtC:, *m.* 70°.
 (CH₂MeC:)₂, *m.* 128.5°.
 MeCOCH₂CH₂MeC:, *m.* 87.5°.

HOOCMeC: , m. 136.5° .
 $\text{HOOCCH}_2\text{CH}_2\text{MeC:}$, m. 119° .
 $(\text{CH}_2)_5\text{C:}$, m. 78° .
 PhCH: , m. 125.5° .
 PhMeC: , m. 109.5° .
 $\text{PhCH}_2(\text{Me})\text{C:}$, m. 84° .
 PhCOPhC: , m. 127° .
 $o\text{-HOC}_6\text{H}_4\text{CH:}$, m. 173° .
 $p\text{-MeOC}_6\text{H}_4\text{CH:}$, m. 125.5° .
 $p\text{-O}_2\text{NC}_6\text{H}_4\text{CH:}$, m. $160\text{--}6^\circ$.
 $p\text{-MeOC}_6\text{H}_4\text{CH}_2(\text{Me})\text{C:}$, m. 91° .
 $\text{C}_4\text{H}_3\text{O}\cdot\text{CH:}$, m. 121.5° .

DITHIOCARBAZIC ACIDS AND SALTS

$\text{H}_2\text{NNHCSSH}$, NH_4 salt, m. 114° dec.; 1049c N_2H_5 salt, m. 124° dec.; 378 MeNH_3 salt, m. 112° dec. 1049c
 PhNHNHCSSH , N_2H_5 salt, m. 110° dec. 1049c
 $\text{Me}_2\text{NNHCSSH}$, m. 112° . 1340

DITHIOCARBAZATES

 RSCSNHNH_2

Methyl-, m. 82° , 50 , 1049c 79° ; 216b Ac., m. 123° ; 783 Bz., m. 170° , 216b 172° ; p -methoxybenzamide, m. 157° ; p -chlorobenzamide, m. 184° . 783
 Ethyl-, m. 40.5° , 1417a oil; Bz., m. 104° ; 216b $4\text{-C}_5\text{H}_4\text{NCO-}$, m. 175° . 1778
 Benzyl-, m. 125° ; Bz., m. 151° . 216b
 $\text{PhCOCH}_2\text{-}$, m. 127° . 1417b
 $\text{HOOCCH}_2\text{CH}_2\text{-}$, m. 114.5° , 1417c 111° . 1121c
 $\text{EtOOCCH}(\text{COMe})\text{-}$, m. 110° . 1417d

 R'NHNHCSSR

PhNHNHCSSPr , m. 125° . 156
 $\text{PhNHNHCSSCH}_2\text{CH}_2\text{COOH}$, m. 131° . 1121c
 $\text{PhNHNHCSSCH}(\text{COMe})\text{COOEt}$, m. 130° . 1417d
 $\text{MeC}_6\text{H}_4\text{NHNHCSSCH}_2\text{C}_6\text{H}_4\text{NO}_2\text{-}o$, o , m. 134° ; p , m. 127° . 217
 $o\text{-O}_2\text{NC}_6\text{H}_4\text{NHNHCSSMe}$, m. 114° . 683
 $\text{PhCOCH}_2\text{PhNNHCSSMe}$, *cis*, m. 93° ; *trans*, m. 100° . 156
 $\text{PhCOCH}_2\text{PhNNHCSSEt}$, *cis*, m. 86° ; *trans*, m. 82° . 156
 $\text{PhCOCH}_2\text{PhNNHCSSPr}$, *cis*, m. 61° ; *trans*, m. 56° . 156

PhCOCH₂PhNNHCSSCH₂Ph, *cis*, m. 75°. ¹⁵⁶
p-MeC₆H₄COCH₂PhNNHCSSMe, *cis*, m. 54°; *trans*, m. 110°. ¹⁵⁶
p-MeC₆H₄COCH₂PhNNHCSSEt, *cis*, m. 77°; *trans*, m. 95°. ¹⁵⁶
 PhNHCOPhNNHCSSEt, m. 150°. ^{216a}

R:NNHCSSMe

PhCH:, m. 157.5° dec. ^{216b}
 PhCH:CHCH:, m. 166°. ¹³⁴⁹
o-HOC₆H₄CH:, m. 196°. ¹³⁴⁹
p-MeOC₆H₄CH:, m. 163°. ¹³⁴⁹
p-H₂NC₆H₄CH:, m. 186°; Ac., m. 224°. ¹³⁴⁹
 2-C₄H₃O·CH:, m. 149°. ¹³⁴⁹
p-C₆H₄(CH:NNHCSSMe)₂, m. 221° dec. ¹³⁴⁹

R:NNHCSSEt

Me₂C:, m. 73°. ^{1417a}
 HOOCCH₂CH₂(Me)C:, m. 118.5°. ^{1417a}
 MePhC:, m. 131°. ^{1417a}
 PhCH:, m. 183.5°. ^{1417a}

R:NNHCSSCH₂COOH

MePhC:, m. 160° dec. ^{1417c}
 PhCH:, m. 168°. ^{1417c}

R:NNHCSSCH₂CH₂COOH

MeCH:, m. 129.5°. ^{1417c}
 Me₂C:, m. 135°. ^{1417c}
 HOOC(Me)C:, m. 160°. ^{1417c}
 PhCH:, m. 160.5°. ^{1417c}

R:NNHCSSCH₂Ph ¹³⁴⁹

PhCH:CHCH:, m. 180°.
o-HOC₆H₄CH:, m. 185°.
p-H₂NC₆H₄CH:, m. 164°.
 2-C₄H₃O·CH:, m. 175° dec.
p-C₆H₄(CH:NNHCSSCH₂Ph)₂, m. 213°.

R':NNHCSSR

PhCH:NNHCSSCH₂COPh, m. 173°. ^{1417b}
 PhCH:NNHCSSCHMeCOOH, m. 147.5°. ^{1417c}

- PhCH:NNHCSSCHPhCOOH, m. 159.5°. ^{1417c}
 PhCH:NNHCSSCH(COMe)COOEt, m. 109°. ^{1417d}
 EtOOCNHNHCSSMe, m. 91°. ¹⁰⁸⁹
 HOOCNHNHCSSEt, amide, m. 192°; ^{216.5} Et ester, m. 91°; ¹⁰⁸⁹
 Benzyl ester, m. 153° dec.; *p*-nitrobenzyl ester, m. 177°
 dec. ^{216.5}
 EtOCSNHNHCSSEt, m. 91°. ^{1417a}
 EtSCSNHNHCSSEt, m. 82°. ^{1417a}
 MeSCSNMeNMeCSSMe, m. 112°. ^{1049c}
 BzNHN:C(SMe)(SEt), m. 47°. ^{216b}
 PhCH:NN:C(SCH₂COOH)(SEt), m. 127°. ^{1417c}
 PhCH:NN:C(SCH₂CH₂COOH)₂, m. 135°; K₂ salt, m. 263°. ^{1417c}
 PhNHN:C(SCH₂C₆H₄NO₂-*p*)(SCH₂Ph), m. 67°; an isomer, m.
 88°. ²¹⁷
 MeC₆H₄NHN:C(SCH₂C₆H₄NO₂-*o*)₂, *o*, m. 134°; *p*, m. 116°. ²¹⁷
 [PhCH:NN:C(SCH₂CH₂COOH)]₂S₂, m. 162.5°; Na salt, m.
 215°. ^{1417c}

AZIDODITHIOCARBONATES

RSCSN₃

- HSCSN₃, electrolytic dissociation *K* at 0° 2.4×10^{-2} , ⁷¹⁸ at 25°,
 2.14×10^{-2} . ¹⁵²⁸
 Methyl-, m. 32°. ⁴⁹
 Benzyl-, m. 64.5°. ⁴⁹
 Ph₂CH-, m. 67.5°. ⁴⁹
 Ph₃C-, m. 132° dec. ⁴⁹
 PhCO-, m. 119–20° dec. ⁴⁹
p-BrC₆H₄CO-, m. 127° dec. ⁴⁹
 CN·SCSN₃, m. 81°. ⁴⁹

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CHAPTER 4.

Carbon Oxysulfide

Introduction

Carbon oxysulfide, carbonyl sulfide, COS, was discovered by Than who obtained it by the action of sulfuric acid on potassium thiocyanate after failing to get it from carbon monoxide and sulfur.²⁶⁶

It is found in the water of some springs.^{68, 96, 159} It may be that the amount so found is but a remnant of a much larger amount which has been hydrolyzed:

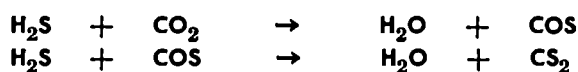


It was looked for but not found in the gases from Vesuvius.⁹⁶

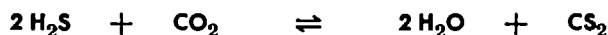
A sample of water gas from a low-sulfur coke contained 2.4 grains per 100 cu.ft.¹² It is one of the sulfur compounds in manufactured gas^{80, 137} and in blast furnace gases.¹⁵⁷

Of the gases obtained by passing carbon disulfide over hot kaolin, 60% is carbon oxysulfide.⁹⁶ It is formed when a mixture of ultramarine and carbon is heated.²⁷ Carbon dioxide and boiling sulfur give it and sulfur dioxide.⁵³ It is contained in the issuing gases when sulfur dioxide is passed over red hot carbon²¹ and when hydrogen sulfide and carbon dioxide are passed through a white-hot porcelain tube.⁹⁶

A review of the chemistry of carbon oxysulfide has been made by Ferm.^{81.5} Equilibrium measurements have been made between 350° and 900°. There are two reactions:



These add up to: ²⁶⁴



The equilibrium has been recalculated by a new method.⁴⁸ Carbon disulfide is oxidised by sulfur trioxide or chromic anhydride to carbon oxysulfide,⁵ and under some conditions by sulfuric acid.¹⁷⁹ It is oxidised by chlorosulfonic acid:⁷⁰



Carbon oxysulfide is obtained by reducing magnesium sulfate with carbon monoxide and by heating magnesium oxide with carbon disulfide.²¹⁵ Some carbon oxysulfide is produced when sulfur dioxide is reduced by incandescent coke.³⁸ When sulfur dioxide and oxygen are blown into an incandescent coke bed, sulfur, carbon monoxide, and carbon oxysulfide are formed.⁶⁷ Below 800° carbon oxysulfide is a by-product in the formation of carbon disulfide from sulfur dioxide and methane.²⁰ Alkali sulfides, heated in carbon dioxide, are converted to carbonates with the evolution of carbon monoxide and oxysulfide along with free sulfur.⁵⁵

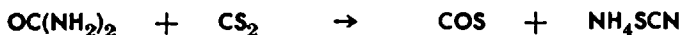
Carbon oxysulfide is formed from phosgene and hydrogen disulfide at 200°.²² Phosgene reacts with cadmium sulfide slowly at room temperature, rapidly at 260–80°,¹⁹⁰ and with metal sulfides in general at higher temperatures:



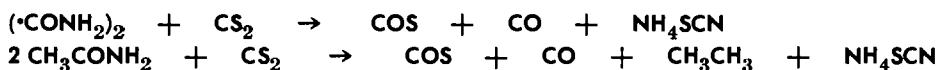
This has been suggested as a means of decomposing sulfides for analysis.⁴⁴

Carbon disulfide and ethyl alcohol passed over hot copper give a mixture of gases among which there is some carbon oxysulfide.⁴⁰ It is obtained from chloropierin and sodium or potassium sulfide.¹⁵⁴ Some of it is produced in the reduction of perchlormethylmercaptan by zinc and hydrochloric acid.¹⁴¹

Urea and carbon disulfide react at 110° to give carbon oxysulfide and ammonium thiocyanate:



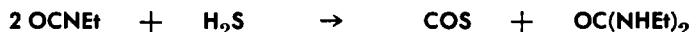
Oxamide and acetamide react at 200°:¹⁵⁸



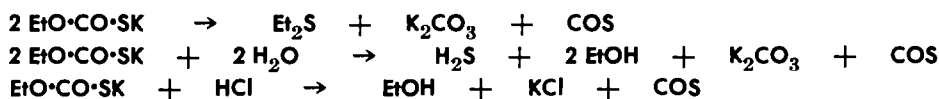
Carbon disulfide is partially desulfurized by an alkyl mercuric hydroxide: ¹⁵³



Ethyl isocyanate and hydrogen sulfide give carbon oxysulfide:



Thioacetic acid decomposes at 300° into carbon oxysulfide and other gases.¹⁵⁸ Carbon oxysulfide is a product of the pyrolysis of aniline nickelodithio-oxalate and of the corresponding cobalt salt.²²² It is formed from an oxime and an isothiocyanate.¹⁹³ It is produced when Bender's salt is heated alone or with water,¹⁹ or in acid solution: ²²⁷



The dry distillation of a sodium or potassium xanthate gives some carbon oxysulfide.⁸⁴ It is a byproduct in the preparation of unsaturated hydrocarbons by the method of Chugaev. The alcohol is converted to the xanthate which is then methylated and pyrolyzed: ^{32, 47, 152, 172, 186, 270, 271}



The pyrolysis of cyclohexylthiocarbanilate yields carbon oxysulfide, cyclohexene, cyclohexanol, and 1,3-diphenyl thiourea.⁵² Some carbon oxysulfide is formed in the ripening of viscose.^{111, 209}

Preparation

For the preparation of carbon oxysulfide powdered potassium thiocyanate is added to dilute sulfuric acid.^{227, 266} Some prefer ammonium thiocyanate.^{109, 141, 280, 290} A solution of 40 g. ammonium thiocyanate in 30 cc. of water is added gradually to a mixture of 290 cc. sulfuric acid and 400 cc. of water at 25°. ⁹⁵ Alkyl thiocyanate and potassium thiocarbamide may take the place of the ammonium thiocyanate.¹²² Ammonium thiocarbamate and hydrochloric acid are recommended.^{258, 259} Carbon oxysulfide may be prepared by bubbling hydrogen sulfide through

an ice-cold water solution of free cyanic acid.²³⁸ Thiourea, an isomer of ammonium thiocyanate, gives carbon oxysulfide when it is heated with an organic acid:



The gas is freed from carbon dioxide and hydrogen sulfide by 33% caustic soda solution, and from carbon disulfide by charcoal, and dried by calcium chloride, sulfuric acid, or phosphorus pentoxide.⁶⁵

Than attempted to prepare carbon oxysulfide by passing carbon monoxide and sulfur vapors through a hot porcelain tube but was unable to isolate it from the products. The same reactants have been brought together under other circumstances without obtaining the desired results.⁹⁸ However, it was obtained in this way by Salomon.²²⁷ In an all-glass container kept at 302°, 99% of the enclosed volume of carbon monoxide combined with sulfur.¹⁶² This method has been used for the preparation of carbon oxysulfide containing radioactive sulfur, oxygen, or carbon.¹⁷⁸ Sulfur vapor gives carbon oxysulfide with either carbon monoxide or dioxide. With the latter, sulfur dioxide is produced also.⁴⁵ Sulfur is said to combine with carbon monoxide in the presence of activated carbon.¹²¹ It has been proposed to manufacture carbon oxysulfide from carbon monoxide and sulfur dioxide¹⁸³ or hydrogen sulfide,^{1, 1.5} from carbon dioxide and hydrogen sulfide,¹⁹⁶ or from mixtures of hydrocarbons, air, or carbon dioxide, and sulfur^{1, 1.5} under suitable operating conditions.

Properties

The properties of carbon oxysulfide are, in general, intermediate between those of carbon dioxide and carbon disulfide.¹⁴⁵

It melts at -138.2° ,²⁵⁸ -138.79° ,¹³⁶ -138.84° .⁵⁰ The heat of fusion is 1129.8 ± 1.0 cal. per mole.¹³⁶ The melting point is far lower than those of the symmetrical carbon dioxide (-56.4°) and carbon disulfide (-111.85°). It boils at -47.5° ,¹⁰⁹ $-50.23^\circ \pm 0.05$,¹³⁶ -42° at 760 mm. The heat of vaporization is 4415 ± 4 cal.,¹³⁶ 4534 ± 8 cal.⁸⁷ The heat¹³⁴ and entropy²⁵⁶ of vaporization have been calculated. Its boiling point is much nearer to that of carbon dioxide (-78°) than to that of carbon disulfide (46°).

The density is 1.24 at -87° ,²⁵⁸ 1.073 at 0° and 0.986 at 32.2° . Liquid densities of COS from -100° to $+100^{\circ}$ have been determined and are represented between -100° and 50° by the equation:²⁰¹

$$\rho = 1.049 - 0.0029t - 6.76 \times 10^{-6}t^2$$

The coefficient of expansion ($0-32.2^{\circ}$) is 0.002710, γ (2.3°) is 13.00 dynes/sq.cm. and its temperature coefficient ($2.3-17.8^{\circ}$) 0.1626 dynes/sq.cm./ 1° . The parachor is 111.1, calc. 119.4. The liquid is not associated.²⁰⁵ The coefficient of expansion at constant pressure has been determined.¹²²

At 0° and 760 mm. one liter of the gas weighs 2.7125 g. and at 25° 2.4849 g.¹³⁶ At 20° water dissolves 0.54 volume of the gas; at 22° alcohol dissolves eight volumes and toluene fifteen.²⁵⁸ At 14° toluene dissolves 17% of its weight of the gas which it gives off on heating. This is a convenient way of storing the gas.²⁹⁰ The solubility of COS in certain oils and mixtures has been determined.^{7, 170} A saturated ketone solution of COS gas has a good solvent action for vinyl chloride polymer and its copolymers.¹⁸⁴ The absorption coefficient for water is: 1.333 at 0° , 0.835 at 10° , 0.561 at 20° and 0.403 at 30° .²⁹⁴ Water at 13.5° dissolves 0.8 volume of the gas. The critical temperature and pressure are 105° and 63 kg./sq.cm.¹⁰⁹ Other authors give $102.2^{\circ} \pm 0.2^{\circ}$ for the critical temperature.²⁰¹ The viscosity in C.G.S. units $\times 10^{-4}$ is 1.135 at 0° , 1.200 at 15° , and 1.554 at 100° . Sutherland's constant was calculated to be 330. The mean collision area of the molecule from kinetic theory is 1.06×10^{-15} sq.cm.²⁴⁵ The collision diameter for COS mixed with NH_3 is given.^{118, 246} The theoretical molecular heat is found to agree closely with the experimental.³⁵

The determination of the crystal form proved to be difficult.²⁸³ It has been accomplished by the study of a powder diagram.²⁷⁹ Solid carbon oxysulfide is rhombohedral with $a = 4.08$ A. and $\omega = 98^{\circ} 58'$. There is one molecule in the unit cell. The calculated d is 1.526 and the measured 1.52. The atoms form chains along the trigonal axes with $\text{C-O} = 1.10$ A., $\text{C-S} = 1.96$ A., and $\text{O-S} = 2.78$ A., according to X-ray data.²⁷⁹ Viscosity determinations have shown $\text{C-O} = 1.30$ A. and $\text{C-S} = 1.68$ A.,²¹³ while electron diffraction measurements give $\text{C-O} = 1.16$ A. and $\text{C-S} =$

1.56 Å.,^{61, 64} C-O = 1.13 Å. and C-S = 1.58 Å.,^{73, 202} with C-S = 1.54 Å. in carbon disulfide.⁶¹ The figures from microwave investigations are close to those from electron diffraction.²⁵⁴ From Raman spectra the distances are C-O = 1.04 Å., and C-S = 2.38 Å.⁶³ Compressions and phase diagrams for solid COS are given for pressures up to 10,000 atmospheres at low temperatures.²⁵⁷

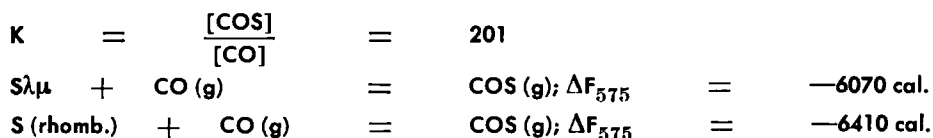
The dissociation energies of the triatomic molecules, OCS, OCO, and SCS have been discussed.²⁸⁹ The influence of electron energy on the dissociation of the COS molecule into ions was studied on a mass spectrometer.¹⁸¹ A study of the higher ionization potential has been made.²⁶² Force constants for COS have been calculated from the fundamental vibrational frequencies,²⁹¹ from infrared²⁸⁰ and from microwave^{132, 280} frequencies. Studies have been made of the bond stretching of the COS molecule.^{176, 182, 223, 267} Other physical means have been used to investigate structure.^{41, 189} Values for thermal conductivity, viscosity, and diffusion in the gas phase are given for COS.⁴ Calculations have been made for its sound velocity and absorption coefficient per unit wave length.²³ The refraction and dispersion have been measured and compared with those of hydrogen sulfide and sulfur dioxide.¹²⁰

The dielectric moment is 0.650×10^{-18} and the structure may be rectilinear like carbon dioxide.²⁹⁶ The dielectric constant of COS was measured at 9400 Mc/sec. over a range of pressures and temperatures.²⁸ Measurements of the dielectric constants and dipole moment have been made by the beat-frequency method.¹²⁶ The total dipole of COS is 0.72 debye with C-S contributing 0.09 debye and O-C contributing 0.63.²⁹³ The diamagnetic susceptibility of COS and the necessary atomic susceptibility constants and bond dispersions have been calculated by Pauling's equation.⁴⁹ By electron diffraction it is proved to be linear.⁷³ The same conclusion is drawn from the electron interference.²⁶

Berthelot gave the following data on the heat of formation:²¹

COS gas	+	H ₂ O	+	water	=	CO ₂ (solution)	+	H ₂ S (solution)		
								+	20,200 cal.	
C (diamond)	+	O	+	S (solid)	=	COS (gas)	+		19,600 cal.	
CO	+	S (solid)			=	COS (gas)	-		6,200 cal.	
CO	+	S (gas)			=	COS (gas)	-		3,600 cal.	
2 COS					=	CS ₂	+	CO ₂	+	40,000 cal.

Free energy of formation and heat of formation ^{146, 147} as well as the log of the equilibrium constant of formation ¹⁴⁶ are given. The thermodynamic constants have been calculated; ²¹⁶ they have been determined and plotted as free-energy/temperature diagrams. ²¹⁸ The heat of combustion is 11,590 cal. per mole. ¹⁰⁹ Data on the free energy of formation are: ¹⁶²



Equilibrium conditions for the reaction have been studied. ^{162, 163, 217, 218}

In carbon disulfide the strength of the C-S bond is 131.7 Kg.cal. but for splitting sulfur off from carbon oxysulfide it is only 76.9 which is only a little more than half of the 131.7. Hence the sulfur is bound only one half as strongly as in carbon disulfide. ⁷⁵ The free energies of formation of CS₂(1) and COS at 298.1°K are +15.24 and -40.48 kg.cal. ⁶⁰ When carbon oxysulfide burns with a deficiency of oxygen the C-S bond is severed preferentially. ²⁰³ From the spectrum both of the bonds appear to be double bonds. ¹⁶⁶ The central carbon atom shares four electrons with each of the other two. ²¹³ The resonance structure has been compared with those of carbon dioxide and disulfide ⁴⁹ and the extinction coefficient measured. ⁸⁵ The discharge spectrum has been studied. ^{86, 203} Carbon oxysulfide has a complicated spectrum with three fundamental frequencies. ²⁰⁶ The thermodynamic properties ¹³⁵ and methods of deducing them from the spectra, ⁶ the formation and dissociation energies ²³¹ and atomic structure ^{69, 148} of groups of compounds, including carbon oxysulfide, have been discussed. The carbonyl accounts for 13% of the polarity of COS. ²⁸⁷ For COS a calculated value of -39.80 ¹⁹⁷ for free energy of formation is obtained from thermal data.

The gas imperfection of carbon oxysulfide has been evaluated and compared with that of other gases. ⁶² The heat capacity of carbon oxysulfide from 0° to 3000° has been determined, ¹⁴⁷ and data for the empirical heat capacity equation for COS are given. ²⁵¹ The experimental heat capacity data for COS are compared with the results of calculations based on a semitheoretical method suggested by Lord. ³³

The ultraviolet absorption spectrum of gaseous carbon oxysulfide shows a continuous absorption from 2550 Å. far toward the ultraviolet, corresponding to the dissociation into carbon monoxide and sulfur.¹⁶⁷ A linear structure is indicated.¹⁸⁵ At low pressures the absorption begins at 1600 Å.^{85, 210} and breaks into several diffuse bands indicating different electronic transitions.^{112, 210} A rounded absorption maximum occurs at 2250 Å., and a sharp maximum at 2800 Å.²¹¹ In ethanol solution the absorption is from 2200 Å. to 3100 Å.³¹ The ultraviolet absorption spectrum of COS has been compared with those of other compounds containing the C:S group.²⁷⁷ Experimental data on the ultraviolet absorption spectrum have been compared with the calculated.²⁸⁷

The infrared spectrum of COS has been examined;¹³ it and the Raman spectrum were obtained in the 3–25 μ region by using a spectrograph of high resolving power.¹⁶⁰ The lack of symmetry of the molecule is demonstrated by the complicated infrared spectrum. The molecule may be linear or triangular.⁹ An analysis of the spectrum shows that the structure of the molecule is intermediate between that of carbon dioxide and that of carbon disulfide. The structural formula is apparently O:C:S.⁹ Fifteen infrared bands have been measured;¹⁴ fourteen bands were observed between 1 and 5.5 μ .² The atomic polarization of COS has been calculated from infrared intensity.^{110, 292} Coriolis perturbation and molecular constants have been derived from some infrared COS bands.²²⁶ The resonance structures of carbon oxysulfide, dioxide, and disulfide have been compared.⁴⁹

The Raman frequencies are 524, 859, and 2055 cm^{-1} with other lines at 678, 862, 1041, 1383, and 2233.⁶³ The splitting of these bands is in accordance with the theory of Fermi.⁴² The shifts of the Raman bands are not consistent with a linear structure and indicate a valence angle of 152°.²⁸² The light scattering points to the polar nature of the molecule.²⁰⁰ The molecular heat determined by ultrasonic measurements indicates a straight molecule.⁷⁹ The frequency for the maximum absorption of sound is 287 compared with 379 for carbon disulfide.⁹⁰

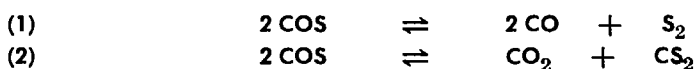
The broadening of the absorption lines of COS under various conditions has been studied.^{3, 81, 130, 164, 207, 247} The relative intensity of the absorption bands,^{11, 39, 174} the Stark effect,^{64, 177, 241, 242, 275} and the relaxation time^{144, 230, 236, 285} have been observed. The Zeeman effect,^{58, 78, 127} Fermi resonance in the microwave

spectrum,^{168, 169} quadrupole moment,^{273, 274} and the microwave spectroscopy in regions of various wave lengths and under various conditions^{16, 17, 24, 37, 57, 77, 99, 100, 131, 140, 208, 221, 224, 242, 265, 287.5} have also been investigated.

Carbon oxyselenide, COSe, which is quite similar to the oxysulfide, is formed by passing carbon monoxide over heated selenium. It melts at -122.1° , boils at -22.9° at 725 mm., has the density 1.812 at 4.1° , mol.vol. 59.2, and surface tension 19.32 dynes/sq.cm. Its parachor is 126.2, calc. 133.7.²⁰⁴

Reactions

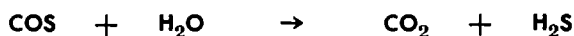
Carbon oxysulfide, when heated, decomposes in two ways:



These reactions are independent: (1) is slow and (2) is rapid. At 950° it is at least 76% dissociated.²⁵⁹ The disproportionation into carbon dioxide and disulfide is exothermic and is catalyzed by various substances, notably by charcoal. The activation energy is 50,000 calories.¹⁷⁵ The rate of the reaction at 450° is sensitive to the nature of the wall, being faster when the vessel is filled with silica. The activation energy is 28,450 calories for the silica surface.²⁰¹ The heat of formation of COS has been calculated to be 33,800 cal. From equilibrium data at 800° and 950° the average value of 49,500 cal. was found for the heat tone of the reaction.²⁶⁰ At equilibrium in mixtures with CO-CO₂ mixed gas in contact with iron and sulfur, the carbon oxysulfide concentration is higher at low temperatures. Equilibria at various temperatures for the formation of carbon oxysulfide from ferrous sulfide and carbon monoxide have been investigated.²⁷⁸ There is no evidence of the formation of carbon monosulfide or sulfur dioxide by heat alone, but by irradiation carbon monosulfide is obtained.¹⁵¹

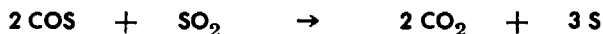
Radioactive sulfur has been used in the study of the structure of the carbon oxysulfide molecule.⁵⁴ The exchange between radioactive and ordinary sulfur at 257° ²⁹⁷ and at 300° in the presence of a Fe—Cr—S³⁵ catalyst¹²³ has been investigated. The equilibrium constants for the exchange have been calculated at 0° , 20° , and 40° .²⁶¹

The hydrolysis of carbon oxysulfide has been studied:³⁶



In alcohol and in the gas phase the bimolecular reaction is several powers of 10 slower than the theoretical as calculated from the observed energy of activation, but in aqueous solution it is somewhat faster than the calculated.²⁶⁹ The temperature coefficient of the hydrolysis reaction is much greater between 0°–50° than at higher temperatures.²¹²

The catalytic¹⁰¹ and photochemical¹⁵⁰ oxidation of carbon oxysulfide have been investigated. A study has been made of the kinetics of the oxidation;⁹⁴ sulfur monoxide has been assumed as an intermediate.⁷¹ The explosion of a mixture of it with oxygen is preceded by an induction period which varies from seconds to minutes, depending on the surface activity of the reaction vessel. Moisture does not change the lower limit but does lengthen the induction period. Careful drying can prevent the formation of the carbon oxysulfide flame.^{18, 268} The explosive limits for mixtures of carbon oxysulfide and oxygen vary with the temperature and the diameter of the reaction vessel.¹⁰⁵ For mixtures with air the limits are 28.50 and 11.90% by volume of carbon oxysulfide.²⁴⁴ Carbon oxysulfide with O₃ shows faint luminescence at about 200° although the mixture is readily explosive.²⁷⁶ It is oxidised slowly but completely by sulfur dioxide at low temperatures:⁶

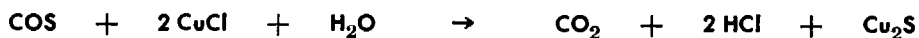


Catalysts and high temperatures speed up the reaction.^{29, 46} It has been proposed to recover sulfur from carbon oxysulfide by oxidation with sulfur dioxide below 350°.²⁸⁶ It is oxidised by sulfuric acid from 150° on up. Palladium is the best of a large number of catalysts tried.¹⁷⁹

Over a catalyst at 200–250°, carbon oxysulfide is desulfurized by hydrogen:²⁴⁹



With nickel sulfide at 150° or above the reaction is of the first order.⁵⁹ Carbon oxysulfide has a deleterious effect on a nickel catalyst in the hydrogenation of carbon monoxide to methane.²⁸⁴ It reacts with cuprous chloride in hydrochloric acid solution:²¹



It reacts when heated with chlorine or with metal chlorides to give phosgene.⁷⁶

With alcoholic potash carbon oxysulfide reacts like carbon disulfide in the formation of xanthates: ^{19, 288}

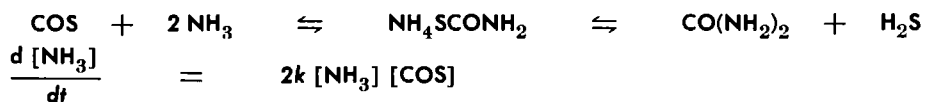


This reaction was used to prove the identity of carbon oxysulfide from carbon monoxide and sulfur with that obtained by the action of sulfuric acid with a thiocyanate.²²⁷ It had been suggested that the two might be isomeric, (CO)S and (CS)O.¹⁴⁹ With alkali cellulose, carbon oxysulfide reacts about two hundred times as rapidly as does carbon disulfide.¹¹³ At 0° the reaction is 45% complete within forty minutes.¹¹⁴ An extensive study has been made of the viscoses prepared from mixtures of carbon oxysulfide and disulfide. The addition of carbon oxysulfide lowers the viscosity of the viscose.²⁰⁹ From ethyl chloroformate and sodium mercaptide the same ester is formed as from Bender's salt and ethyl iodide.²²⁷ When both alcohol and mercaptan are present with alkali the carbon oxysulfide combines with the alcohol to give Bender's salt, EtO·CO·SK.¹¹⁶

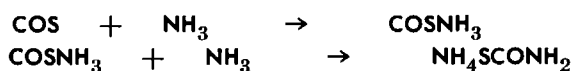
Carbon disulfide reacts very slowly with ammonia but the oxysulfide gives the thiocarbamate quickly: ^{21, 96, 155, 232}



The reaction has been studied kinetically in gas phase at 0–50°. It is approximately of the second order:



$k = 2.31 \times 10^{-3}$. The temperature coefficient is small, only 0.90 for 20°. It goes in two stages: ²³⁹



Urea, thiourea, and thiocyanate have been obtained from the water solution of the ammonium thiocarbamate, NH₄SCONH₂. The formation of urea from ammonia and carbon dioxide, or carbon oxysulfide, has been considered from the viewpoint of thermodynamics. The yield from the oxysulfide should be twice that from the dioxide and besides the reaction is faster.^{142, 143} A commercial method for the manufacture of urea has been proposed ⁸⁸ and the chemical engineering factors have been worked out.⁴³ The limitation is the availability of carbon oxysulfide.

When added to an alcoholic solution of an amine and caustic potash, carbon oxysulfide forms a thiocarbamate, $\text{EtNH}\cdot\text{CO}\cdot\text{SK}$.¹³³ Passed into an ether solution of benzylamine, it gives $\text{PhCH}_2\text{NHCOSH}\cdot\text{H}_2\text{NCH}_2\text{Ph}$, which separates as shiny leaflets. With aniline in hot ethanol, the 1,3-diphenylurea is formed at once.¹⁰⁶ The diphenylurea is also obtained from aniline in water containing hydrogen peroxide.¹⁰ 1,3-Diarylureas can be prepared in excellent yields by treating a monoprimary arylamine with carbon oxysulfide in the presence of an alkali catalyst.^{4,5} Dimethylamine and carbon oxysulfide give dimethylammonium dimethylthiocarbamate, $\text{Me}_2\text{NCOSNH}_2\text{Me}_2$; piperidine and morpholine give analogous compounds.¹⁹⁸ Ethylene urea is prepared by heating carbon oxysulfide with ethylene diamine until the evolution of H_2S ceases.¹⁷¹ With diamines in which the amino groups are separated by longer carbon chains, the products are linear polymers.^{56, 138, 187, 187.5} Carbon oxysulfide is said to react with ethyleneimine and its homologs.¹²¹ Condensation with an α -aminonitrile gives a thiazoline¹⁹⁹ and with *o*-aminophenylacetonitrile, a thiazole.⁵¹

With a Grignard reagent a thiol acid is formed: ²⁵



Polymers of high molecular weight are formed from dimethylketene and carbon oxysulfide.^{66, 255} Condensation polymers may be treated with carbon oxysulfide to raise their molecular weights.¹²¹ With phenol, carbon oxysulfide forms a clathrate compound the structure of which has been studied.^{252, 253} With nitrogen as a diluent, carbon oxysulfide with CoF_3 yielded a solid, nearly pure SF_6 , and a liquid mixture of SF_6 and COF_2 .²⁴³ In a current of carbon oxysulfide between 90° and 370° , lead oxide is converted to the sulfide.²³³ Carbon oxysulfide is said to cause the disintegration of concrete,^{89, 91} and is antagonistic to lead tetraethyl in gasoline,¹⁶⁵ but in liquefied petroleum gas does not cause corrosion.¹⁸⁸ Traces of it have a favorable effect on the formation of iron carbonyl.¹¹⁵

Removal from Gas Mixtures

The removal of carbon oxysulfide from illuminating gas and from gases which are to be used in chemical reactions, such as the synthesis of ammonia, is important. Activated carbon,^{97, 117,}

²²⁹ to which ammonia may be added,^{8, 125} has been recommended. It has been proposed to remove carbon oxysulfide from gases by moist amines²⁶³ or by amines in solution; piperidine,^{194, 248, 263} diethylamine,⁷⁴ ethanolamine,^{34, 128, 139, 281} and diethanolamine¹⁹¹ have been claimed. Alkali may be added to ethanolamine solution^{34, 128} or ammonia and a copper salt to the piperidine.²⁶³ The ethanolamine may be on a solid adsorbent.²³⁵ Bauxite alone¹⁰⁸ or impregnated with a solution of copper thiomolybdate²⁷² may be used. Sodium plumbite²³³ and cadmium salts²³⁴ on carriers and contact masses of iron oxide and alkali^{15, 72} are said to be efficient. Other methods are: Solution in water at 15 atmospheres³⁰ or in aqueous^{180, 192} or alcoholic^{102, 191} caustic alkali, conversion to hydrogen sulfide,²²⁸ adsorption by silica gel,⁹³ oxidation,^{4,3} by a special porous cement catalyst,⁶ by anion exchange resins,²²⁰ by passage through a hydroforming unit,¹²⁹ and by treatment with reactive metals dissolved in molten salts, oxides, hydrates, or metals.¹²¹ The subject of removal of carbon oxysulfide from gases has been discussed.^{92, 119, 161, 240}

Determination

Considerable work has been done on methods for the determination of carbon oxysulfide in the presence of other sulfur compounds as may be found in manufactured gas and contaminated air, viz., by adsorption in dilute alkali followed by titration procedures,^{107, 156} by similar methods requiring special apparatus,^{124, 173, 219} by selective absorption,^{195, 214} by polarographic,^{209, 237} and spectrophotometric³¹ methods. The liberation of palladium from palladium chloride has been proposed for the detection of carbon oxysulfide.¹⁰³

It is a curious fact that carbon oxysulfide is rapidly taken up by dilute solutions of caustic soda, 33% per minute for an 8% solution, but only 2% per minute by a 30% solution. This is used in the volumetric analysis of mixtures of carbon monoxide and dioxide, carbon oxysulfide, and other gases. The measured sample is brought in contact with 1 cc. of 30% sodium hydroxide and the volume read each minute for several minutes. Add 4 cc. of water and read the volume every ten minutes for an hour to get the carbon oxysulfide. Finally add 1 cc. of 30% caustic potash solution and read the volume every day for several days to get the carbon disulfide.^{258, 259}

Carbon oxysulfide may be hydrolyzed by potassium hydroxide and the sulfide ion determined.^{104, 211, 250, 295} The sulfur can be weighed as palladium sulfide.⁶⁸ With barium hydroxide, barium carbonate and sulfide are formed.⁸⁴

Carbon oxysulfide is absorbed by sodium or potassium hydroxide solution to form carbonate and sulfide. It is probable that the thiocarbonate, $\text{KS}\cdot\text{CO}\cdot\text{OK}$, is the first product and that this is hydrolyzed: ^{21, 288}



It can also be determined by conversion to H_2S by passing it with hydrogen over aluminum oxide at 900° .⁸² Explosion with oxygen has been recommended.²²⁵ Absorption in a 7.5% calcium chloride solution containing 1% of ammonium hydroxide has been advised.⁶

Physiological

Carbon oxysulfide affects the nervous system and causes dizziness.¹⁴¹ Rabbits exposed to a concentration of 0.24% suffered convulsions and disturbances of the respiratory centers while 0.32% was fatal in a short time. Frogs showed much more resistance, probably on account of their lower oxygen requirements. In a concentration of 1.5% for an hour they suffered paralysis of the respiratory center but recovered.⁸³ The blood does not show absorption bands characteristic of carbon monoxide.¹⁰⁹ In a concentration of 0.89%, mice died in 45 seconds; of 0.29%, in 90 seconds; and of 0.12%, in 35 minutes; 0.09% did not seem to be harmful.¹⁴²

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CHAPTER 5.

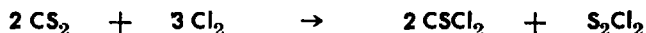
Thiophosgene



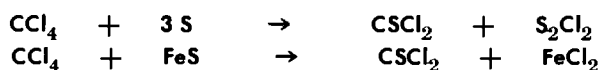
Introduction

Thiophosgene, also called thiocarbonyl chloride, is the sulfur analog of phosgene. From it may be prepared ester chlorides, esters, thioesters, ester amides, ureas, and substituted ureas. Compounds prepared from thiophosgene will, of course, contain thiocarbonyl instead of carbonyl. The reactions of thiophosgene are, in general, analogous to those of phosgene but are usually more sluggish.

Thiophosgene was discovered by Kolbe in 1843. Chlorine and carbon disulfide standing in a flask for some days reacted:



He made it also by shaking carbon disulfide with a mixture of manganese dioxide and hydrochloric acid and by passing carbon tetrachloride and sulfur dioxide through a hot tube.⁴³ It was obtained along with other products by Gustavson from carbon tetrachloride and sulfur in a sealed tube at 180–200°.³⁰ James obtained it by chlorinating methyl thiocyanate.³⁵ Carbon disulfide was passed over hot bone black in the hope of getting carbon monosulfide which could be chlorinated by antimony pentachloride, but this failed.³² A small yield can be obtained by heating carbon tetrachloride with sulfur and somewhat more with ferrous sulfide: ²⁶



Some of it is obtained in the electrolytic chlorination of carbon disulfide³⁴ and also in the chlorination of $(\text{Cl}_2\text{HC})_2\text{S}$.²⁷

Preparation

Thiophosgene is customarily prepared by the removal of chlorine from perchlormethyl mercaptan:



Various reagents have been used for this purpose. Rathke seems to have been the first to make it by abstracting chlorine from perchlormethyl mercaptan by a metal:⁵³



Klason used tin for this reduction.⁴¹ Ever since, tin and stannous chloride, with hydrochloric acid, have been the preferred reducing agents.^{14, 21, 23, 28, 31, 36, 37, 40} Zinc and hydrochloric acid may be used;³³ potassium sulfite is recommended:¹⁴



Iron has been avoided since it catalyzes the formation of carbon tetrachloride but it is said to give an 80% yield if properly used.²⁶ An organic compound has been recommended for the removal of the chlorine.⁵⁰ Thiophosgene is produced by treating perchloromethyl mercaptan with a hydro-aromatic compound in the presence of a Friedel-Crafts catalyst.⁴⁹ An 80% yield is said to be obtained by the dropwise addition of perchlormethyl mercaptan to tetralin at 200°. ²⁴ Catalytic removal of the chlorine by hydrogen has been claimed.²⁵

Properties

Thiophosgene boils at 73.5° and has d_{15} 1.5085, $d_{9/4}$ 1.53951, n_D^{20} 1.54424.¹² Equations for heat capacity together with constants for these equations have been given.^{42, 60} The free energy of formation, heats of formation and combustion, heat capacity, and enthalpy have been determined.⁴² It mixes with the ordinary organic solvents but is insoluble in water. There have been investigations on its electron diffraction,^{10, 20} dipole moment,¹⁵

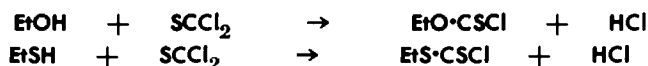
Raman spectrum,⁶¹ and on its ultraviolet,^{31.5} infrared,^{31.5, 46, 48} and long wave⁴⁵ absorption. Studies have been made of the electronic spectrum and molecular vibrations of the thiophosgene molecule.^{11, 20} Data for the intensity, bond moments, molecular structure, and spectrum are given,⁴⁴ also for the matrices and force constants for the nonplanar modes of thiophosgene.⁶²

Thiocarbonyl Fluoride, SCF₂

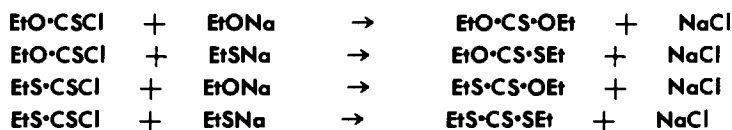
This compound is prepared by the action of sulfur on trifluoriodomethane at 205°.³ It boils at -46° and freezes at -134°.⁶⁴

Reactions of Thiophosgene

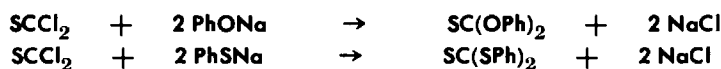
Thiophosgene is far less reactive than phosgene. It is attacked by water very slowly and reacts with only one molecule of an alcohol or mercaptan:



In the presence of alkali the second chlorine is replaced: ^{9, 41, 55}



It reacts well with sodium phenate and thiophenate: ⁵²



In the presence of alkali, *o*-mercaptophenol and thiophosgene give benz-1,3-oxathiole-2-thione, m. 97–8°.²⁹ From thiophosgene and the sodium salt of a dialkyl dithiocarbamate the product is S(CSNR₂)₂.⁶⁵

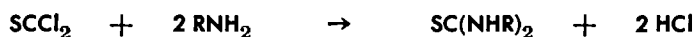
With ammonia the product is ammonium thiocyanate. Perhaps ClCSNH₂ is an intermediate:



With primary amines the reaction goes in two stages:

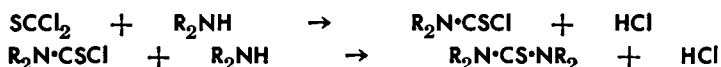


This is an excellent method of making alkyl and aryl isothiocyanates and will be taken up in another volume. The amine, or its hydrochloride, is added to an excess of the thiophosgene. Otherwise a dialkylthiourea results: ^{22, 53}



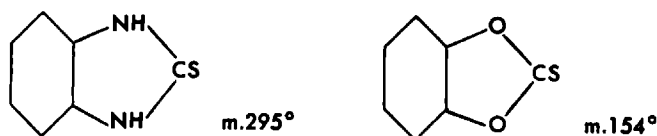
2-Aminopyridine and thiophosgene in benzene give about 60% of 1,3-di-2-pyridylthiourea.⁵⁶

With dialkyl or diaryl amines the primary product is the thio-carbamine chloride which may react with a second molecule of the amine:



The second reaction is favored by an excess of the amine or by the presence of alkali.^{7, 8}

With *o*-phenylene diamine and pyrocatechol cyclic compounds are formed: ²



Phenyl benzoyl diazomethane and thiophosgene give a cyclic compound.¹¹ A cyclic trithio-carbonate is obtained with 2,5-dithiol-1,3,4-thio-diazole.⁵⁴ 2-Mercapto-oxazolines are formed from thiophosgene and certain amino alcohols.⁴ Thiophosgene reacts with malonic ester. The product melts at 177–8° and is probably polymeric. In the presence of aluminum chloride thio-benzophenone can be made:

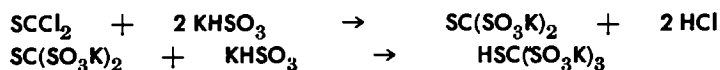


When thiophosgene is passed over ammonium chloride at 400°, disproportionation takes place: ⁵



This decomposition is catalyzed by iron at moderate temperatures.¹⁷

Thiophosgene reacts with potassium bisulfite in two stages: ¹⁴

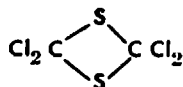


The same product is formed from potassium sulfite.¹ The reaction with nickel carbonyl has been studied in the hope of preparing carbon monosulfide but results were not conclusive.^{19, 47} With NaF in cyclic tetramethylene sulfone at 210–250° thiophosgene gives (F₃CS)₂, F₃CSCl, and other materials.⁶³ With ethylene oxide several products are obtained; these may be assumed to be derived from the initially formed 2-chloroethyl chlorothioformate.³⁸ Thiophosgene is oxyluminescent.¹⁶

Thiophosgene has some value in fumigation; ⁵¹ it has a greater anti-oxygenic effect on benzaldehyde than phosgene.¹³

Dithiophosgene

Light changes thiophosgene into a dimer and breaks down the dimer to the monomer.⁵³ These changes may be followed by measurements of the magnetic susceptibility.⁶ That it is a dimer is shown by cryoscopic measurements, but the molecular refraction did not fit the formula, Cl₃C·S·CCl₃:S, which had been proposed.¹² The dimer is a solid the melting point of which is variously given as 112.5°, 116°, and 119°. This photopolymerization is similar to that of anthracene.⁵⁷ The ring structure ⁵⁹ has been confirmed by the infrared spectrum: ³⁹



Dithiophosgene reacts with aniline to form Cl₂C(S)₂CNPh, m. 70°. With water it gives Cl₂CS₂CO and with alcohol C₂S₃Cl₂, m. 58–9°.¹⁸

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